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## **ANALYSIS OF THERMAL DEGRADATION OF GLASS REINFORCED PHENOLIC AND EPOXY LAMINATES**

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AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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(Prepared under Contract No. AF 33(616)-8465  
by the Monsanto Research Corporation, Dayton, Ohio,  
Harry S. Wilson, Ival O. Salyer, and J. E. Katon, authors).

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## FOREWORD

This report was prepared by Monsanto Research Corporation under USAF Contract No. AF 33(616)-8465. This contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736005, "Compositional, Atomic and Molecular Analysis." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division. Mr. F. F. Bentley was the project engineer.

This report covers the work on polymer characterization techniques carried out from November 1961 to July 1962.

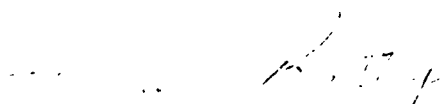
The work was performed at the Dayton Laboratory of Monsanto Research Corporation by I. O. Salyer, H. S. Wilson, A. L. Wurstner and C. D. Fritsch with Dr. J. E. Katon serving as project leader.

## ABSTRACT

Thermogravimetric analyses were made on Resinox SC-1008 silicone modified phenolic resin and 75% glass laminate and compared with similar samples of Epon 828 epoxy resin. The effects of atmosphere, sample geometry, inclusion of sized glass fabric, and instrument variables on the degradation kinetics of these materials were investigated. Kinetic constants were calculated for the materials from thermogravimetric analysis results and an empirical method of kinetic calculations is discussed. The thermal endurance limit of Resinox glass laminate was also calculated.

Differential thermal analyses were carried out on Resinox and Epon laminates and theoretical kinetic relationships were used to facilitate their interpretation.

This technical documentary report has been reviewed and is approved.

  
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# ANALYSIS OF THERMAL DEGRADATION OF GLASS REINFORCED PHENOLIC AND EPOXY LAMINATES

## INTRODUCTION

The behavior and properties of materials subjected to high temperature environments is of particular interest to the Air Force. A number of materials - resins, ceramics, metals, etc. - have been developed for various uses under these conditions and have been characterized to some extent. New materials are being developed at a rapid rate, however, and any method that can be devised for evaluation of the high temperature properties of these materials would be useful. Of particular use are methods that require small amounts of materials and that give data which is directly related to high temperature properties of the material.

One method of characterization which appeared useful for polymeric systems that undergo degradation is thermogravimetric analysis (TGA) and the related differential thermal analysis. These techniques have been previously described<sup>1,2</sup> in relation to simple compounds, but to date have not been generally applied to polymeric systems. It therefore seemed worthwhile to investigate these methods as applied to some commercial high temperature resin systems in an effort to evaluate the information which could be derived and to determine the usefulness of this information for characterizing high temperature properties of polymeric systems.

This project was therefore directed toward evaluation of thermogravimetric and differential thermal analyses for use in characterizing high temperature polymeric systems rather than evaluation of materials as such. Two commercial high temperature resin systems were selected as typical examples of materials to be studied. Therefore this report contains characterization data for these materials, Resinox SC-1008 and Epon 828. The former is a phenolic based resin while the latter is an epoxy type.

## EXPERIMENTAL

All thermogravimetric and differential thermal analyses were run on a modified Aminco Thermograv instrument which has been previously described.<sup>3</sup>

1. Effect of Atmosphere and Sample Geometry Thermogravimetric analyses were run on two cured commercial polymer samples and on 75% glass fabric laminates of these polymers in air, helium and

vacuum. The polymers were tested in the form of finely ground powders, and the laminates were tested intact in samples approximately 1/2"x 1/4"x1/8". The resulting weight loss curves were then normalized to show the rate of loss of polymer content, in percent per degree centigrade. All tests were run at a nominal heating rate of 5°C per minute. Shown in Figures 1, 2 and 3 are TGA curves in air, helium and vacuum for Resinox SC-1008 phenolic resin and a glass fabric laminate containing approximately 25% Resinox resin. Although smaller differences are seen between the curves in helium and vacuum, significant differences between the resin and laminate curves are evident, the laminate in each instance degrading at a greater rate than the polymer. Shown in Figure 4 is a two-step curve, produced by the difference in the rates of degradation in air of Epon 828 epoxy resin and the oxidation of its residual carbon. Apparently the coking value of phenolic resins is so high and the degradation rate in air so low that the two curves merge into one apparent curve. Thus the oxidation of phenolic carbonaceous residue was not discernible as a distinct reaction. Figure 5 is an extremely interesting thermogravimetric analysis curve for I.P. 181 glass fabric sized with 0.3% A-1100 aminopropylsilane. Three distinct regions are apparent, and are believed to correspond to volatilizations as follows:

R.T.-252°C	Loss of adsorbed water
252-352°C	Initial decomposition of size
352-900°C	Degradation of residual organics, lubricants, etc.

2. Effect of Instrument Variables It is apparent that thermogravimetric analyses of practical engineering materials can become quite complex, often involving several over-lapping reactions. The greater the instrument precision, therefore, the more accurate the analysis which can be made of the curve produced. It is imperative that all line voltage changes or internal voltage drops due to furnace regulation, etc., vibrations and instrumental noise be rigidly eliminated in order to obtain faithful reproduction of the thermogravimetric changes. Further, kinetic evaluation of the curves is greatly facilitated by strict time/temperature linearity, i.e., a strictly constant heating rate over the entire range of interest. Slight systematic irregularities can easily lead to erroneous kinetic data. Instruments which depend upon Hookean deflections, i.e., a precision spring and differential-transformer pickup, must be calibrated at each run. Temperature changes of the precision spring can also introduce systematic errors. It is imperative then that excellent vibration damping, electrical isolation of recording instrumentation, and precision calibration be accomplished prior to serious thermogravimetric analysis.

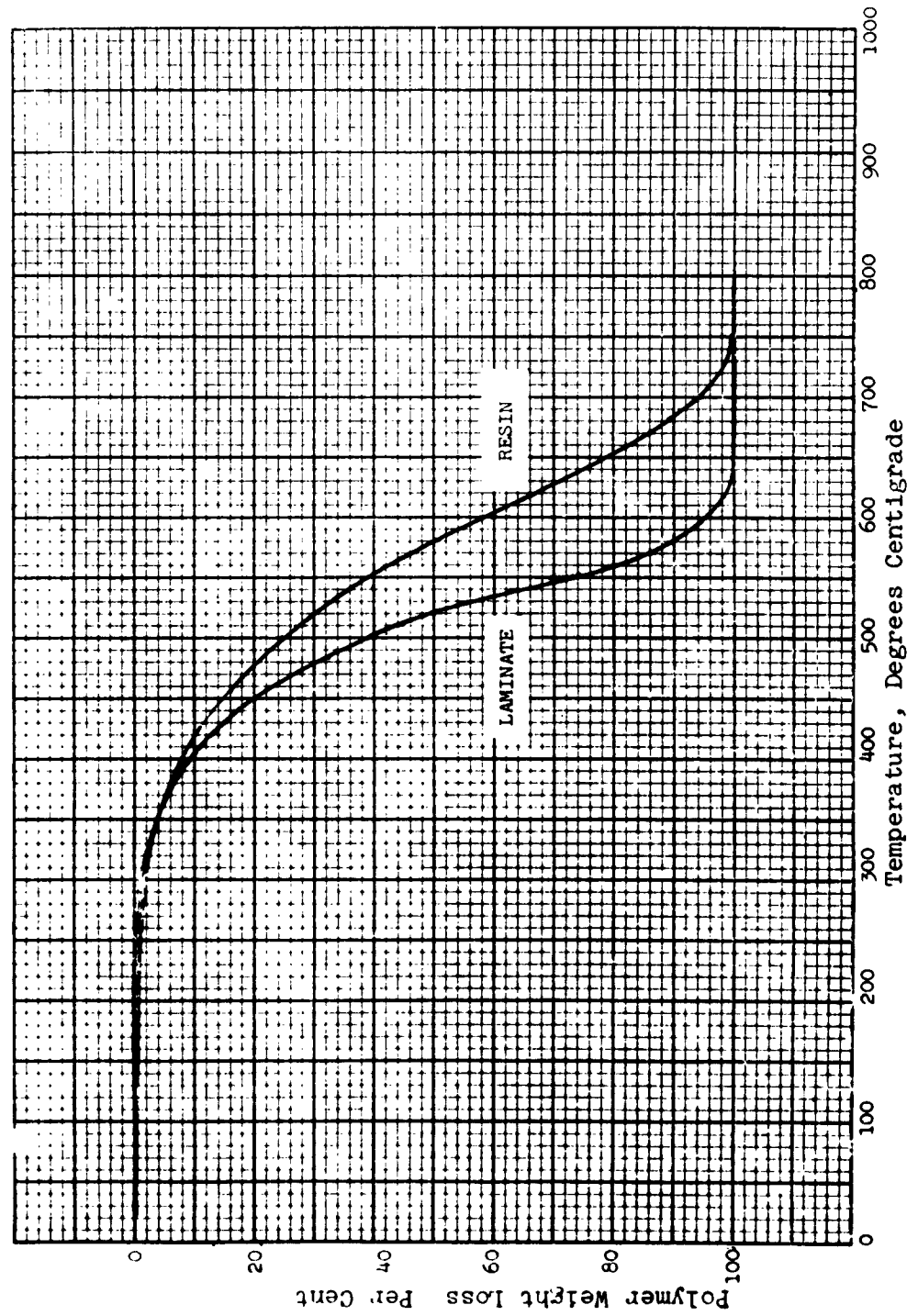


Figure i. Comparison of Thermogravimetric Analyses of Resinox Resin and Glass Laminate in Air

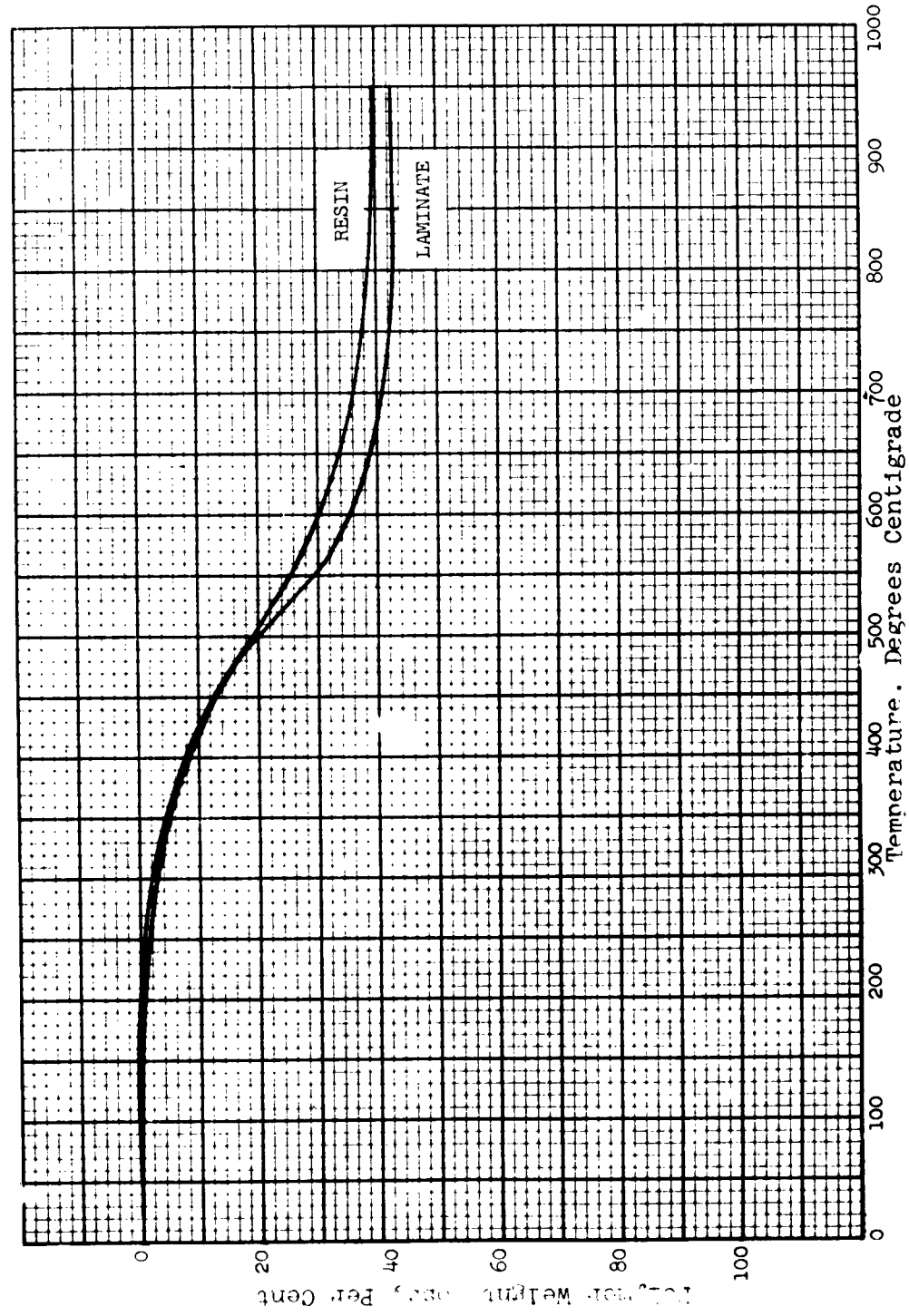


Figure 2. Comparison of Thermogravimetric Analysis of Resin and Glass Laminate in Helium

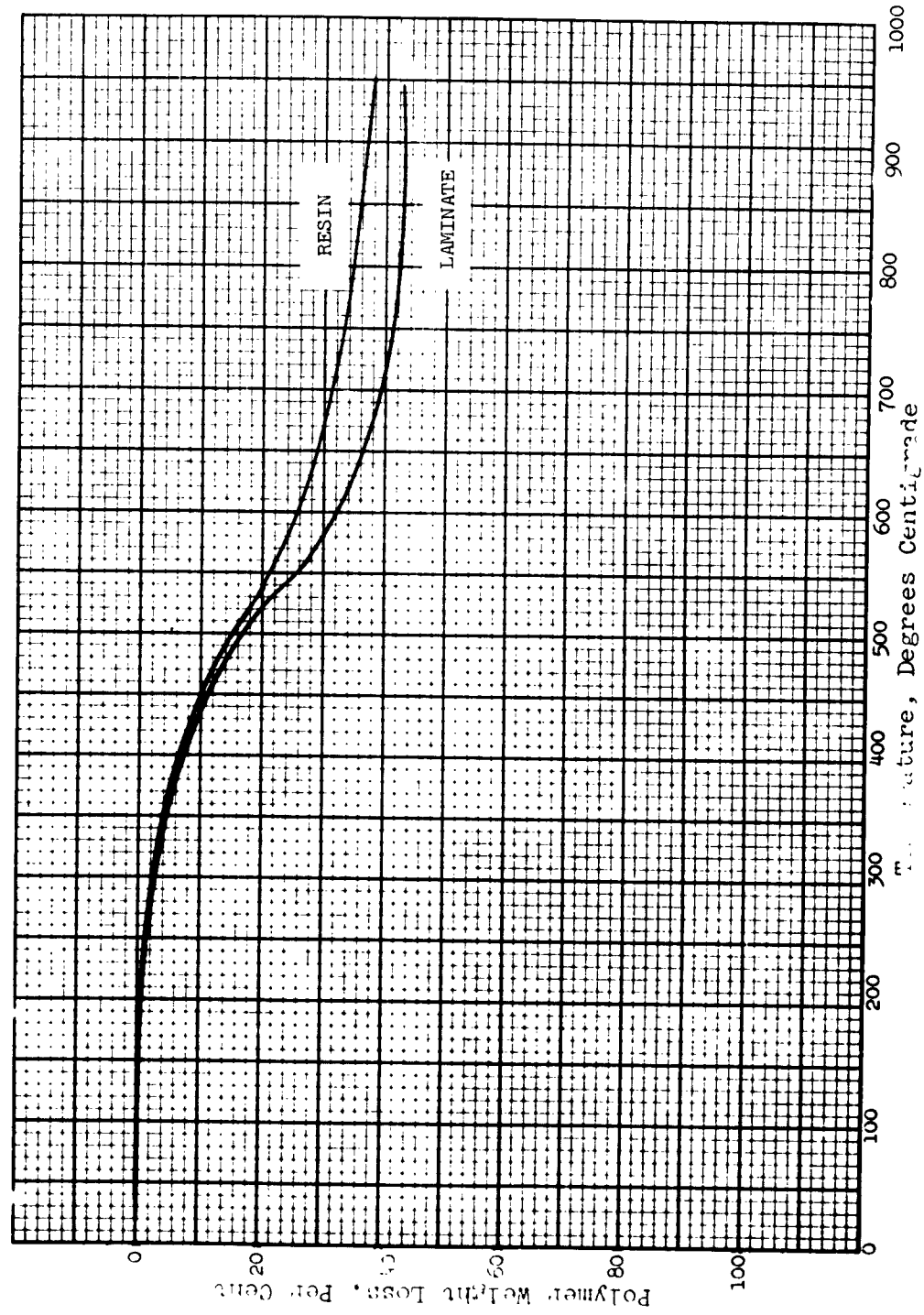


Figure 3. Comparison of Thermogravimetric Analyses of Resinox Resin and Glass Laminate in Vacuum

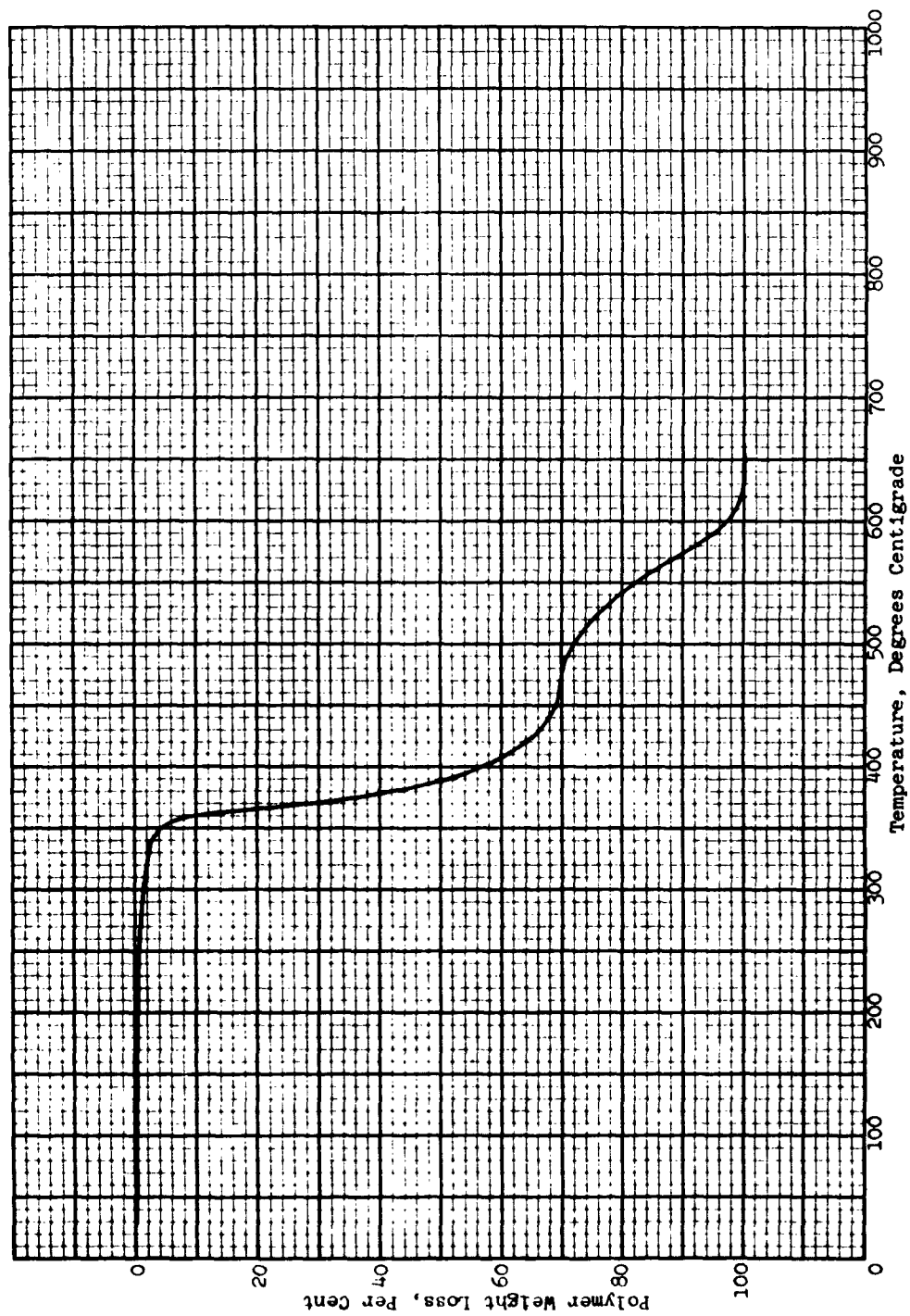


Figure 4. Thermogravimetric Analysis of Epon 828 Resin in Air

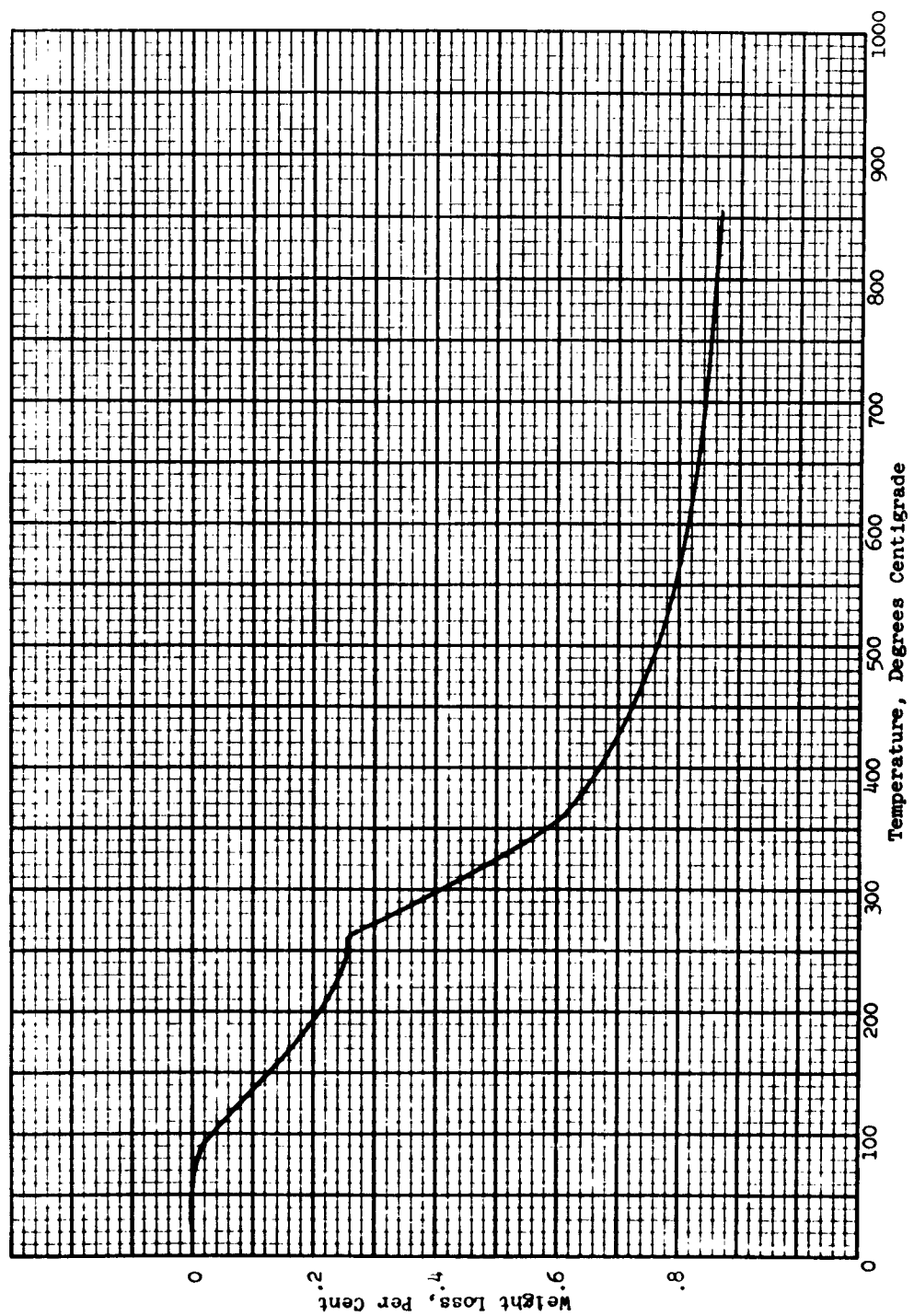


Figure 5. Thermogravimetric Analysis of Glass Fabric and A 1100 Size in Helium



## RESULTS AND DISCUSSION

1. Kinetic Studies The methods of Freeman and Carroll<sup>(4)</sup> and Anderson and Freeman<sup>(5)</sup> were used to treat the thermogravimetric curves of Resinox SC-1008, Epon 828 and the 75% glass fabric laminates of these resins. All tests were conducted at a pressure of 1 mm Hg. Best results were obtained by calculating the parameters at equal increments of  $1/T$ . Increments of  $1 \times 10^{-5}$  to  $1 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$ , depending upon steepness of the TGA curve, were found convenient. Shown in Figure 6 is the TGA curve for Resinox SC-1008 with 5-minute marker intervals. These time-marks were then used to plot Figure 7, weight of reactant vs. time at a nominal increasing temperature rate of  $5^\circ\text{C}/\text{min}$ . The weight of reactant at any time is assumed to be the sample weight minus the carbonaceous residue remaining at the end of the run. This assumption corresponds to the physical situation of one large molecule containing many small units which may be split off on degradation, but which leave the basic network essentially unchanged. This situation is, of course, only an approximation to the true structure, but it is physically reasonable with the systems under consideration. It should be noted that the approximation is valid even if the groups which are split off are part of the original backbone of the network, if the backbone recloses after the leaving groups have been split off. Such time-base curves are of value in obtaining derivatives when the heating rate is not strictly linear. That this is so in the present work may be seen by the slight variation in the size of the hundred degree temperature interval marks. The half-weight loss time was 77 minutes and the half-weight loss temperature was  $536^\circ\text{C}$ . Information obtained from Figures 6 and 7 may then be plotted vs.  $1/T$  as in Figure 8, and this data used for the calculation of the kinetic curve shown in Figure 9. The rather large amount of scatter in these graphs is experimental error whereas consistent deviations from linearity are usually due to other factors, such as initial zero order degradation,<sup>(5)</sup> complex reactions, etc.

The kinetic equations applicable to systems of linearly increasing temperatures are:

$$(1) \quad \Delta \log (dW/dt) = n \Delta \log W_r - \frac{E^*}{2.303R} \Delta(1/T)$$

$$(2) \quad \log Z^* = \log (dW/dt) - n \log W_r + \frac{E^*}{2.303RT}$$

and the Arrhenius equation

$$(3) \quad k = Z^* e^{-E^*/RT}$$

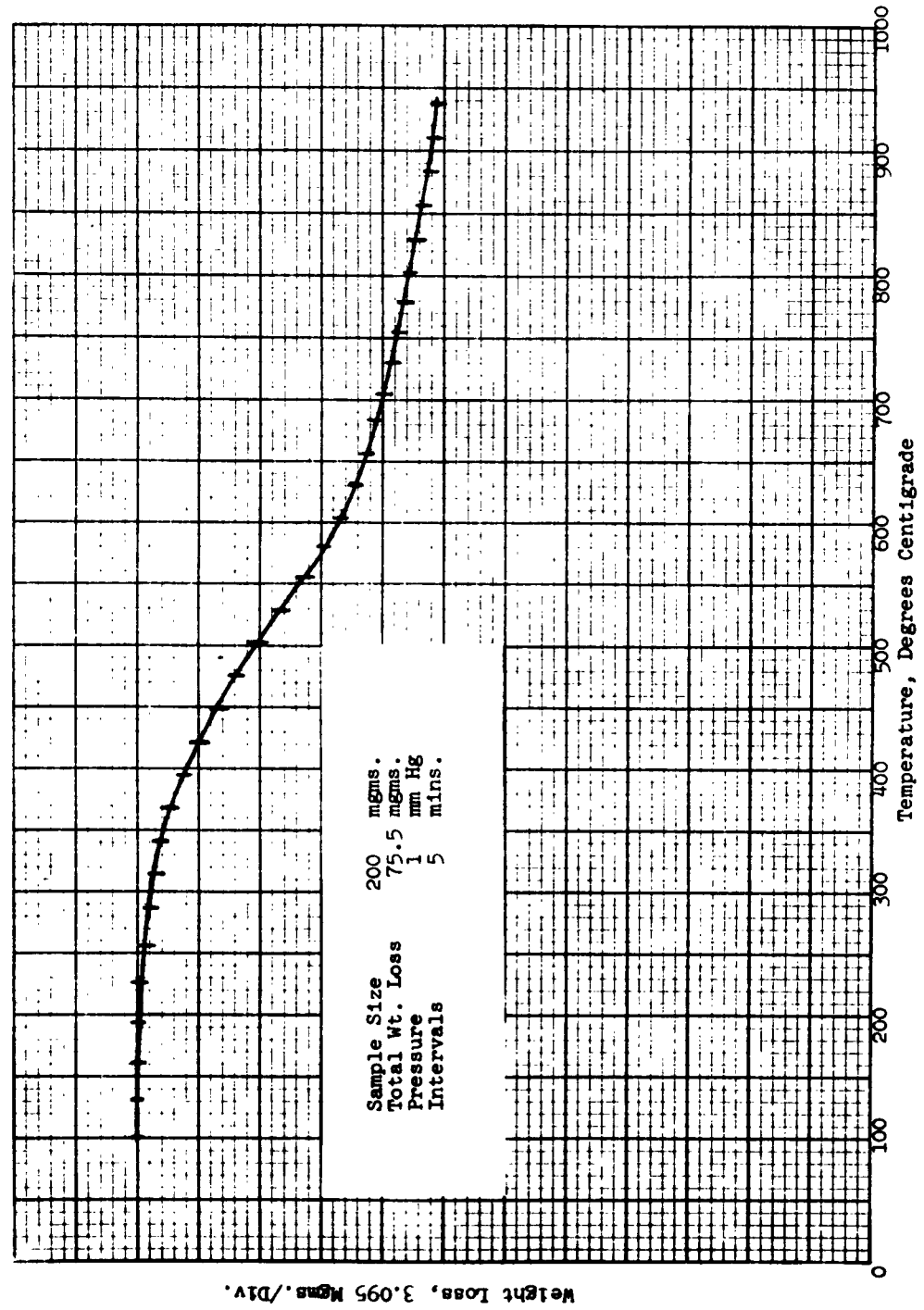


Figure 5. TGA For Degradation of Resinox Resin in Vacuum

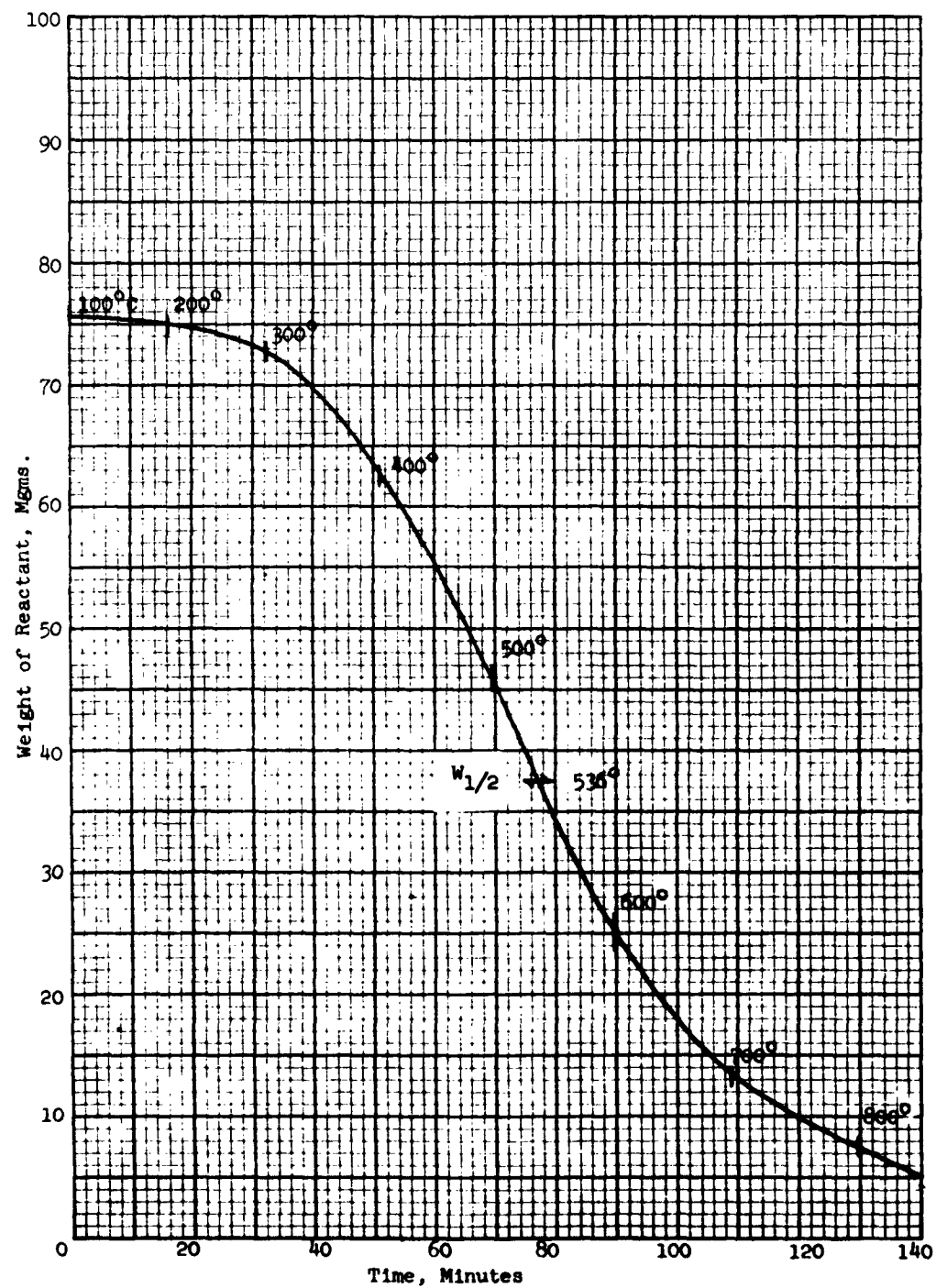


Figure 7. TGA/Time Base for Degradation of Resinox Resin

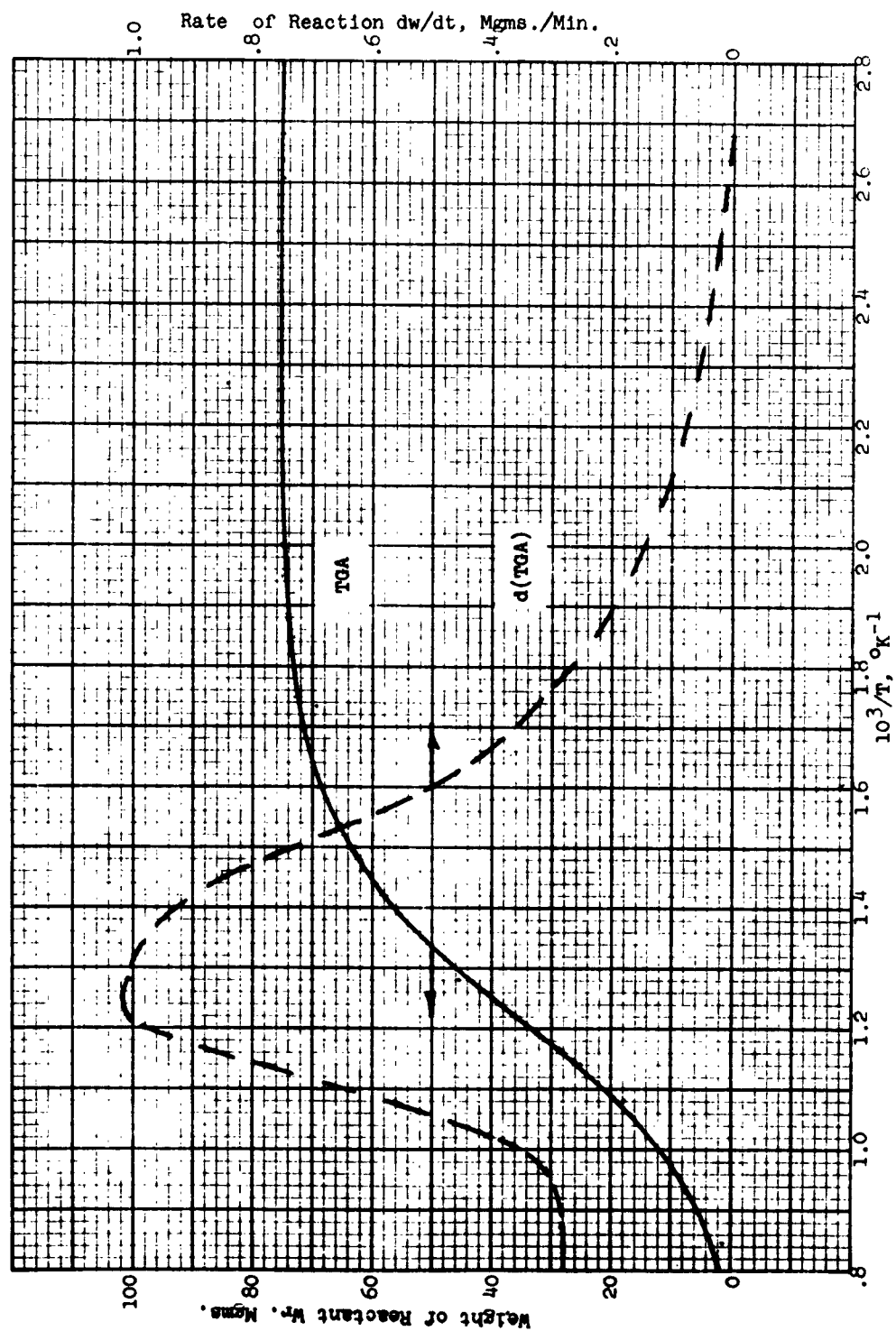


Figure 8. TGA and d(TGA) vs  $10^3/T$  for Degradation of Resinox Resin in Vacuum

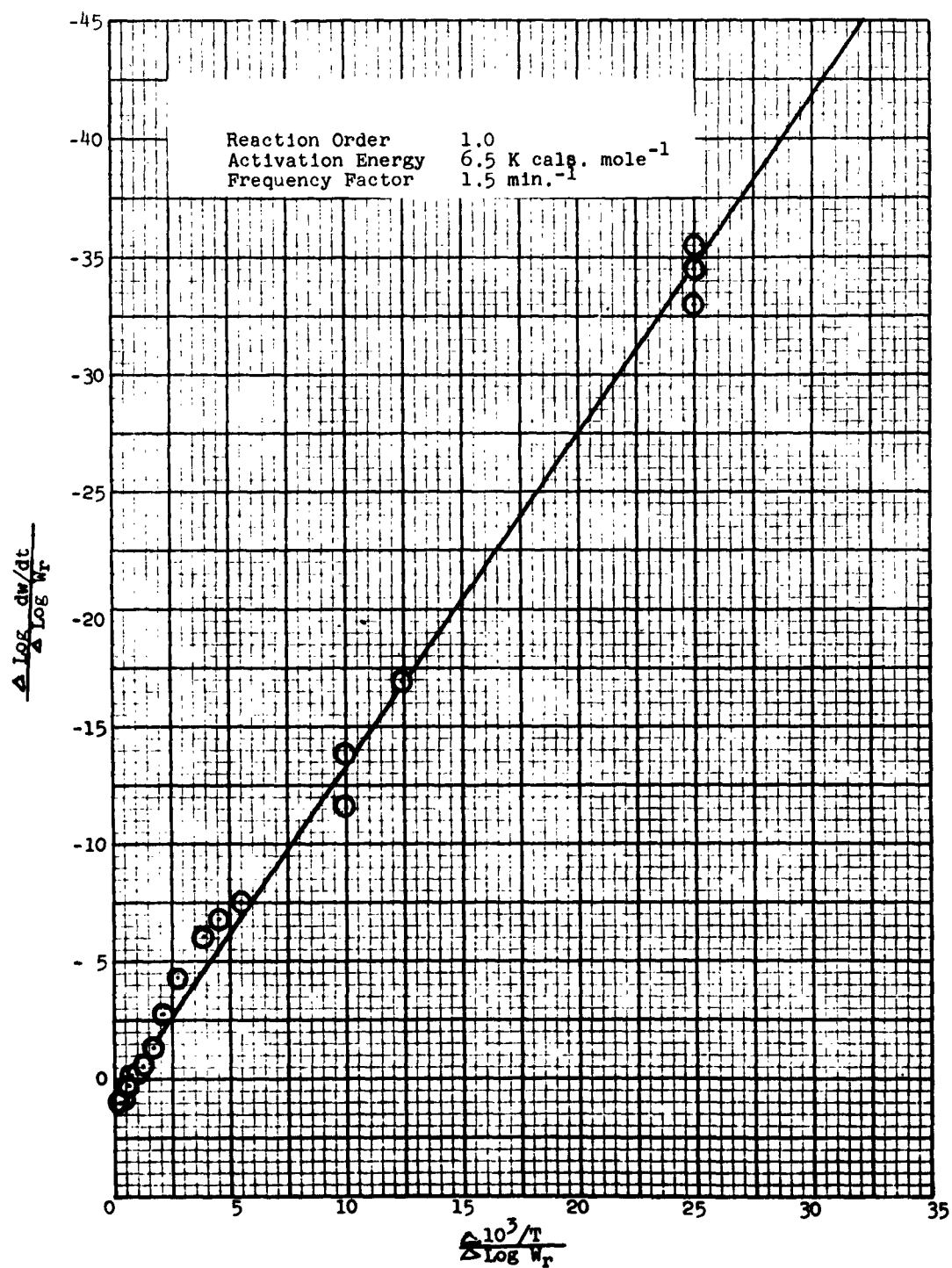


Figure 9. Kinetics of Degradation of Resinox Resin in Vacuum

where

$dW/dt$  = rate of weight loss, mgms./min.  
 $W_r$  = weight of reactant: weight remaining at any time  
less carbonaceous residue, mgms.  
 $E^*$  = activation energy, cal./mole  
 $Z^*$  = frequency factor, min.<sup>-1</sup>  
 $R$  = universal gas constant, 1.987 cal./mole °K  
 $T$  = absolute temperature, °K  
 $n$  = order of reaction  
 $k$  = specific rate constant, min.<sup>-1</sup>

The activation energy is calculated from the slope of the line,

$$(4) \quad E^* = - (\text{slope}) \times 2.303 R$$

and the order of reaction is given by the intercept. To calculate the frequency factor, assumed here to be constant over the temperature range of interest, these two values are substituted into equation (2) above at some convenient temperature such as that corresponding to the cross of the  $W_r$  and  $dW/dt$  curves in Figure 8. The order of reaction is seen to be nominally 1.0, the activation energy an extremely low 6.5 Kcals. per mole and the frequency factor about 1.5 per minute. That such a very low activation energy is reasonable may be appreciated in view of the very gentle slope of the TGA curve, extending to as low as 150°C. Figures 10, 11, 12 and 13 show the corresponding curves for the 75% glass fabric laminate of Resinox SC-1008. The half-weight-loss times and temperatures for the powdered polymer and the 1/2"x1/4"x1/8" sample agree within one minute and one degree, showing their mean equivalent rate constants in the range 25° to 535-6°C to be very nearly the same:

$$(5) \quad \bar{k} = \frac{2.303 \log 2}{t_{1/2}} \approx 9 \times 10^{-3} \text{ min}^{-1}$$

Figures 14-21 show the TGA and kinetic curve for the degradation of Epon 828 resin and laminate. Hardening was accomplished with a stoichiometric amount of m-phenylenediamine; both resin and laminate were cured for 2 hours at 165°C and postcured 3 hours at 225°C. Samples cured at a maximum temperature of 65°C gave almost identical TGA curves. Activation energies of about 35 Kcals./mole agree well with reported(6) values of about 38.7 Kcals./mole. Figure 22 shows isothermal weight loss curves for Epon resin at 350°C and 400°C.

2. Empirical Methods By far the best appearing kinetic curves were obtained by means of an empirical method. Shown in Figures 23 to 26 are the curves obtained for the Resinox and Epon resins and laminates. This type of graph offers three major advantages over other types of kinetic data plots: (1) no tangent measurements are required, as  $dW/dt$  does not appear explicitly in the equation used; (2) both the activation energy and frequency factor are obtainable from the same plot; and (3) the data points are evenly spaced, allowing more accurate visual fitting of a curve to the data points.

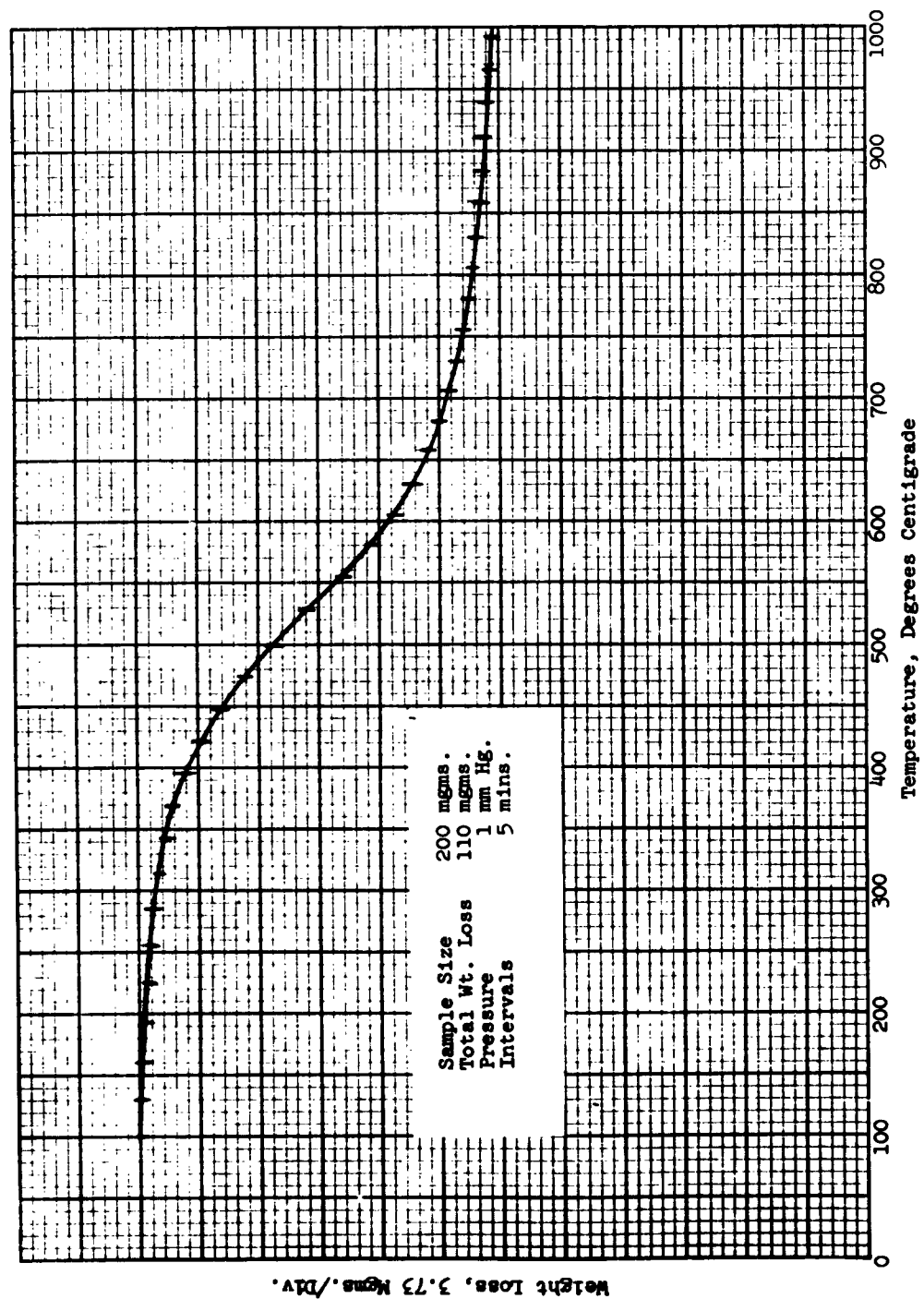


Figure 10. TGA for Degradation of Resin-X Glass Laminate in Vacuum

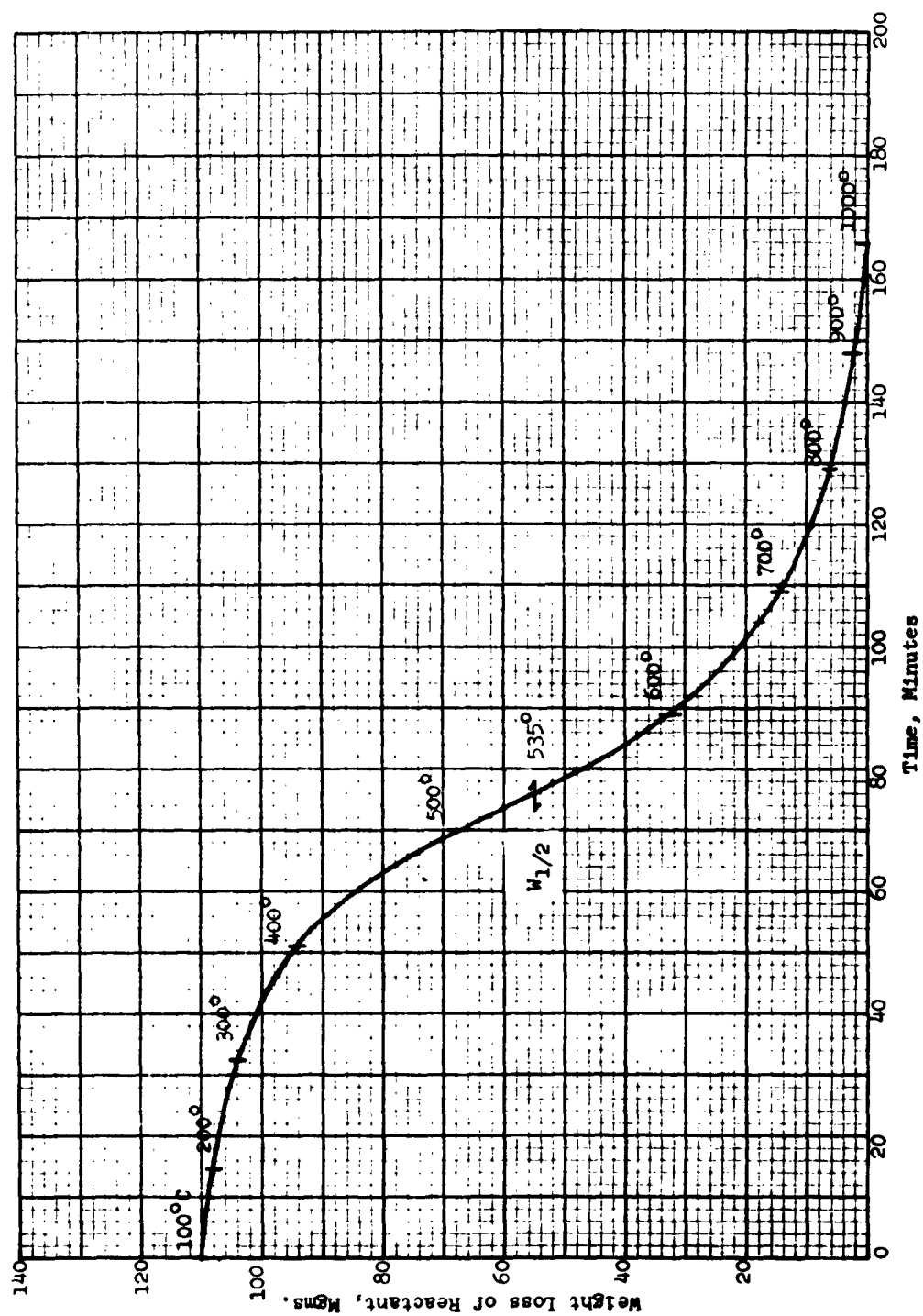


Figure 11. TGA/Time Base for Degradation of Resinox Laminate in Vacuum



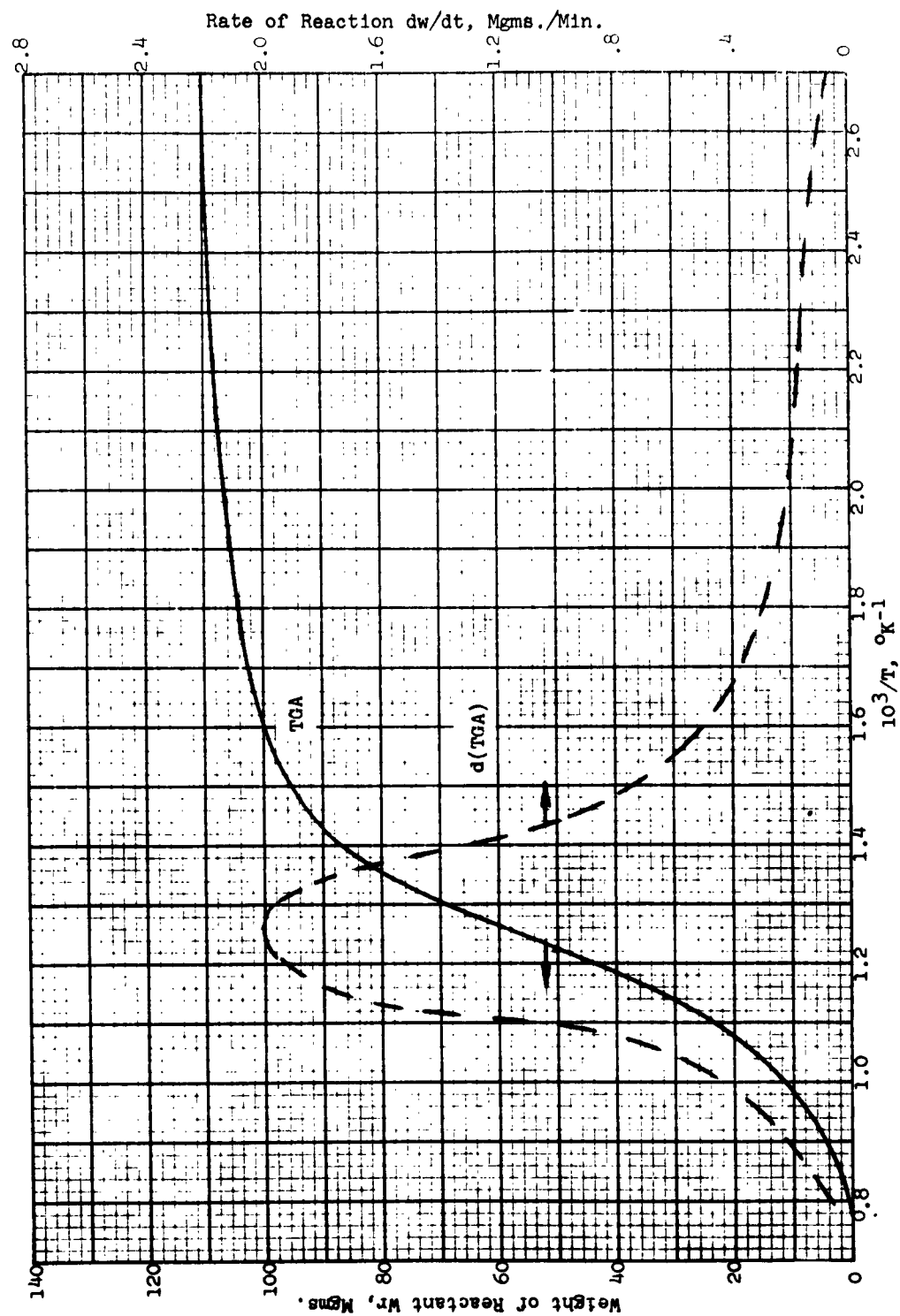


Figure 12. TGA and  $d(TGA)$  vs  $10^3/T$  for Degradation of Resinox Laminate in Vacuum

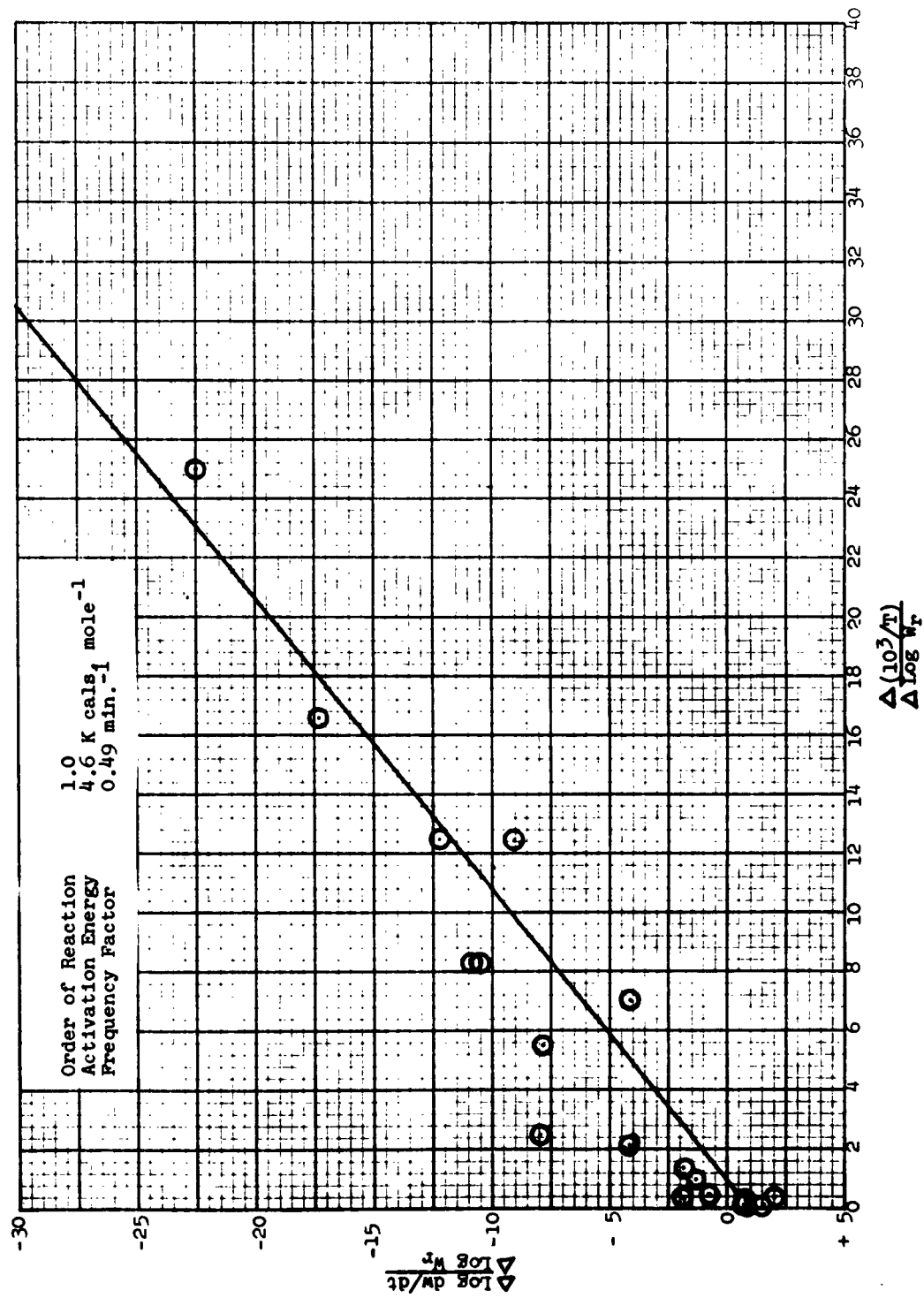


Figure 13. Kinetics of Degradation of Resinox Laminate in Vacuum

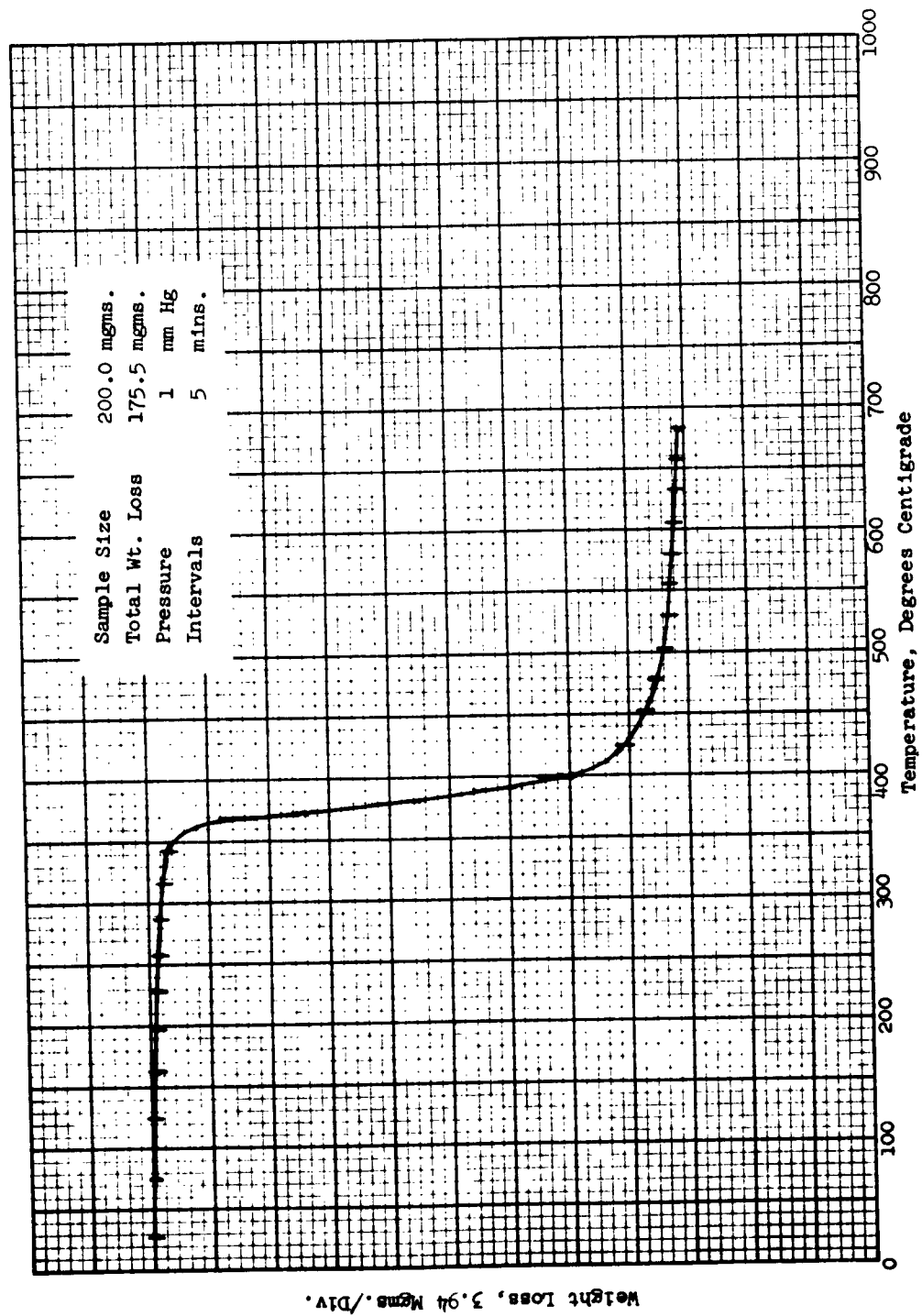


Figure 1. TGA of Degradation of Epon 826 Resin in Vacuum

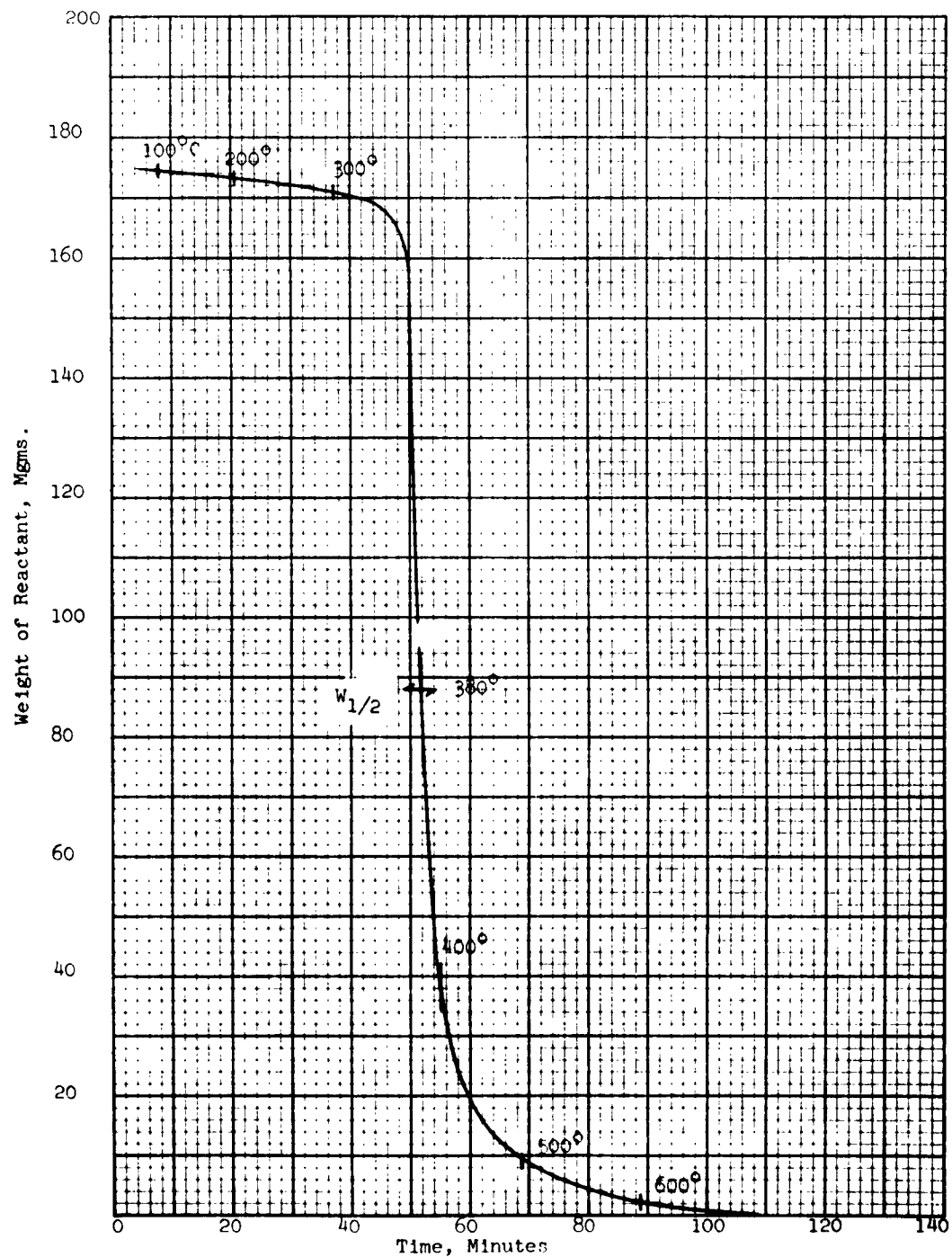


Figure 15. TGA/Time Base for Degradation of Epon 828 Resin

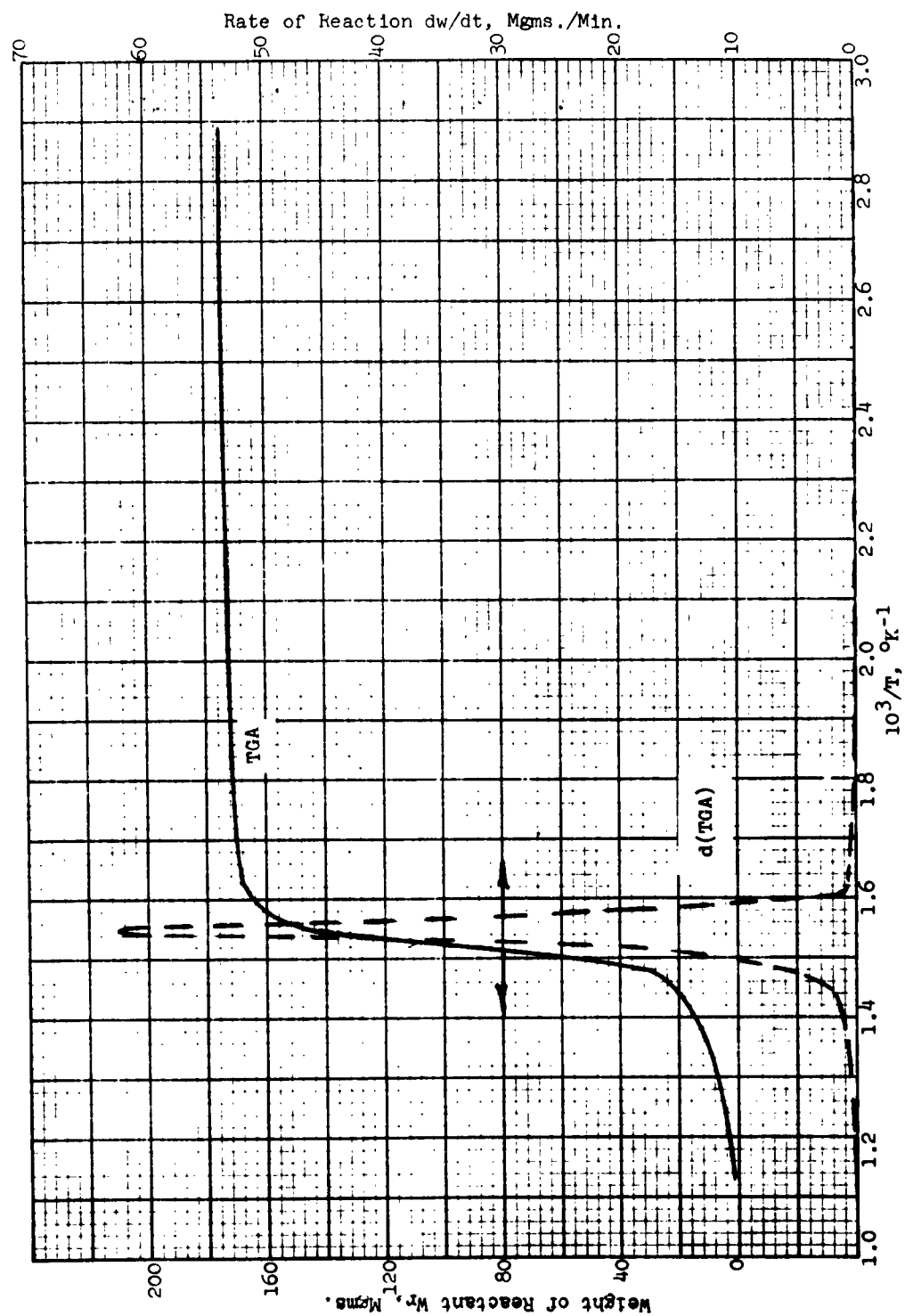


Figure 16. TGA and  $d(TGA)$  vs  $10^3/T$  for Degradation of Epon 828 Resin in Vacuum

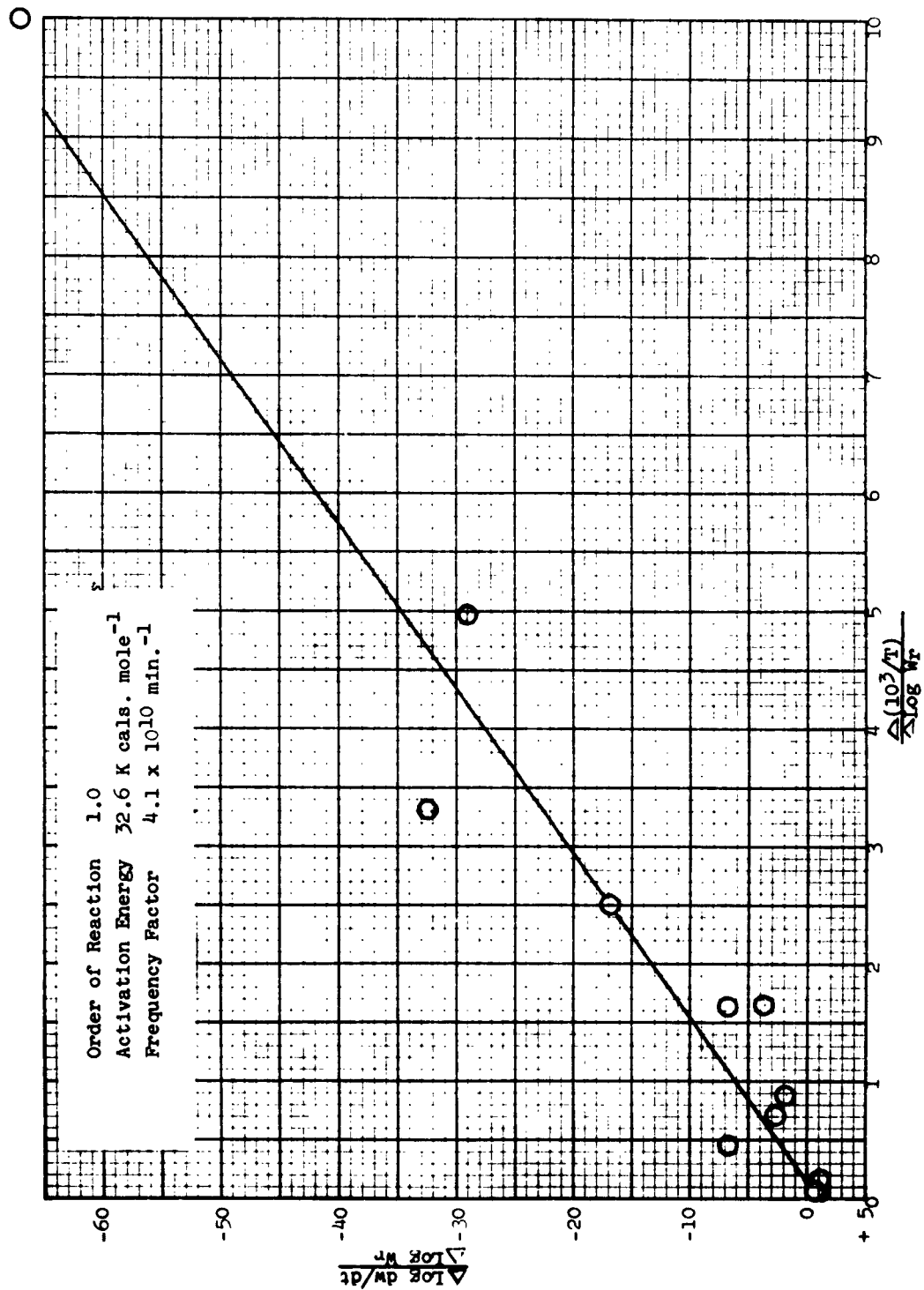


Figure 17. Kinetics of Degradation of Epon 828 Resin in Vacuum

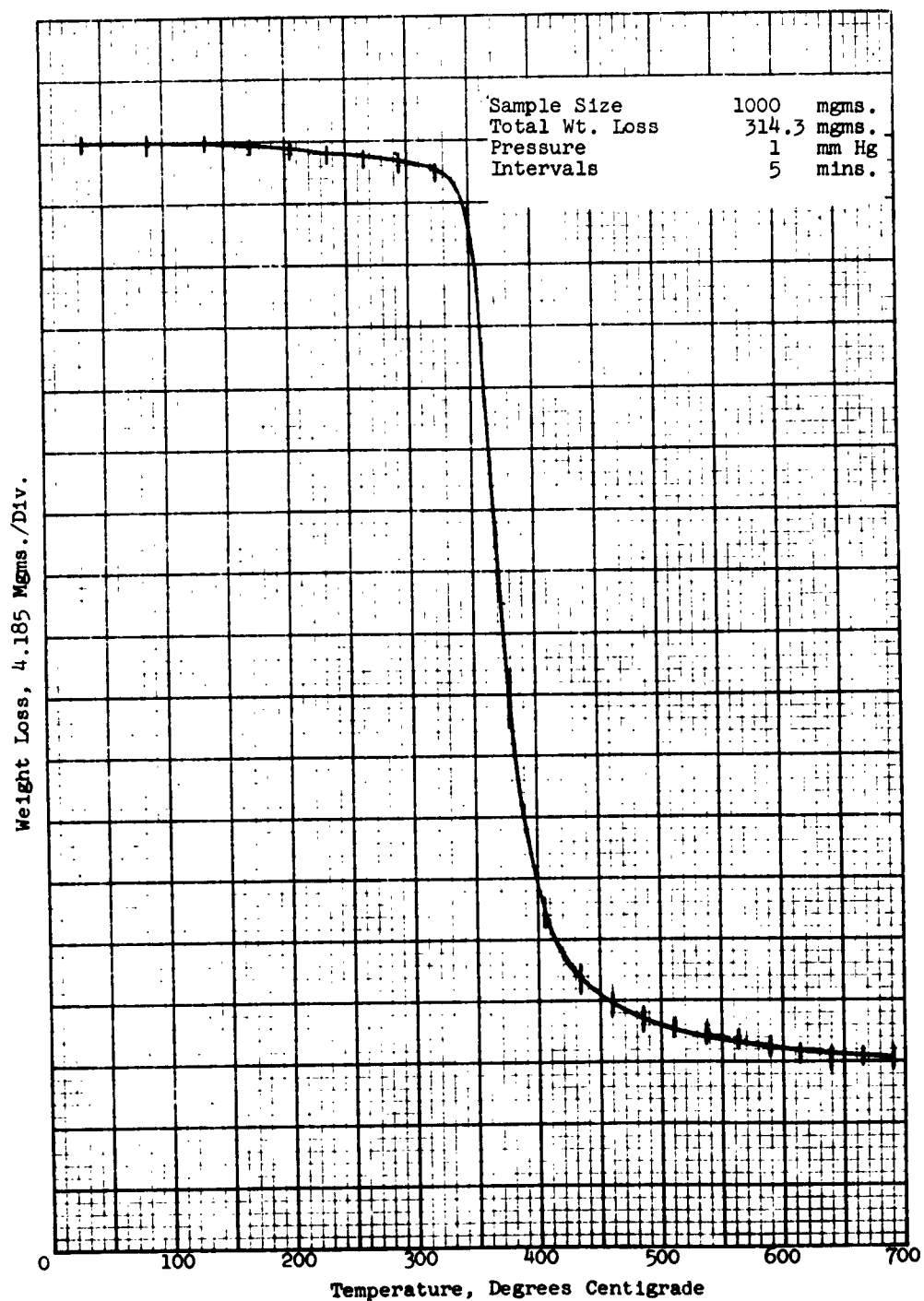


Figure 18. TGA for Degradation of Epon 828 Laminate

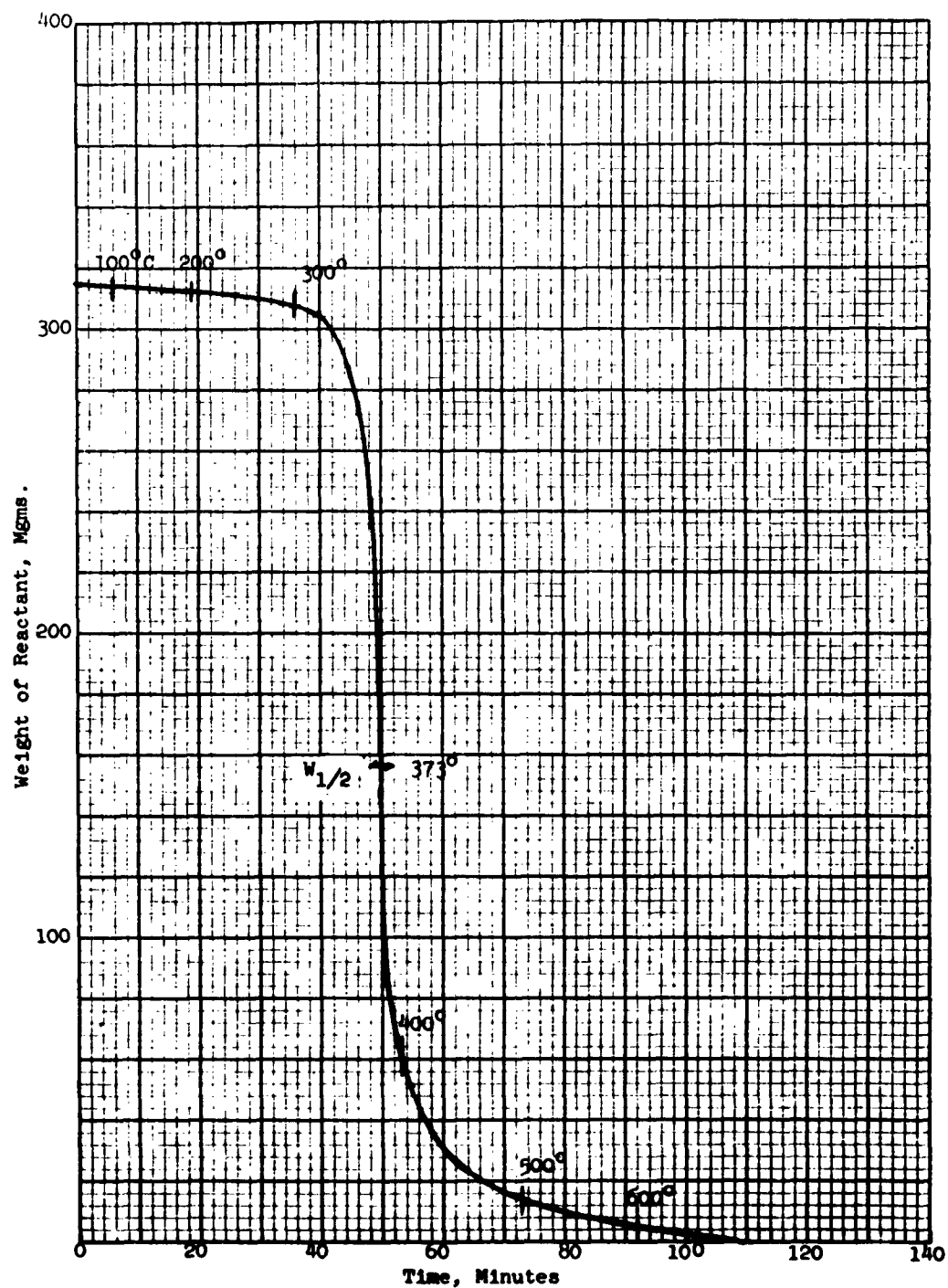


Figure 19. TGA/Time Base for Degradation of Epon 828 Laminate



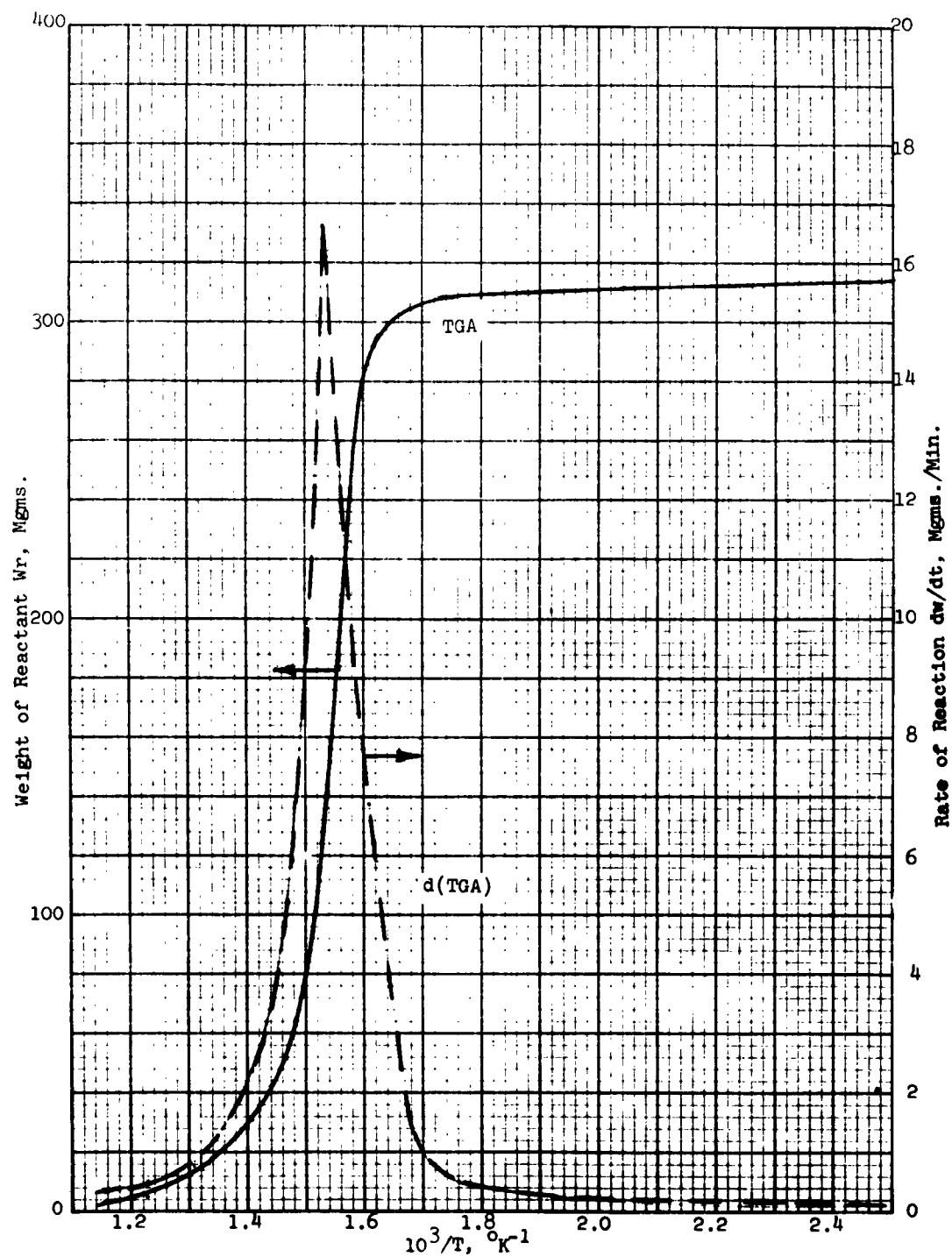


Figure 20. TGA and  $d(TGA)$  for Degradation of Epon 828 Laminate

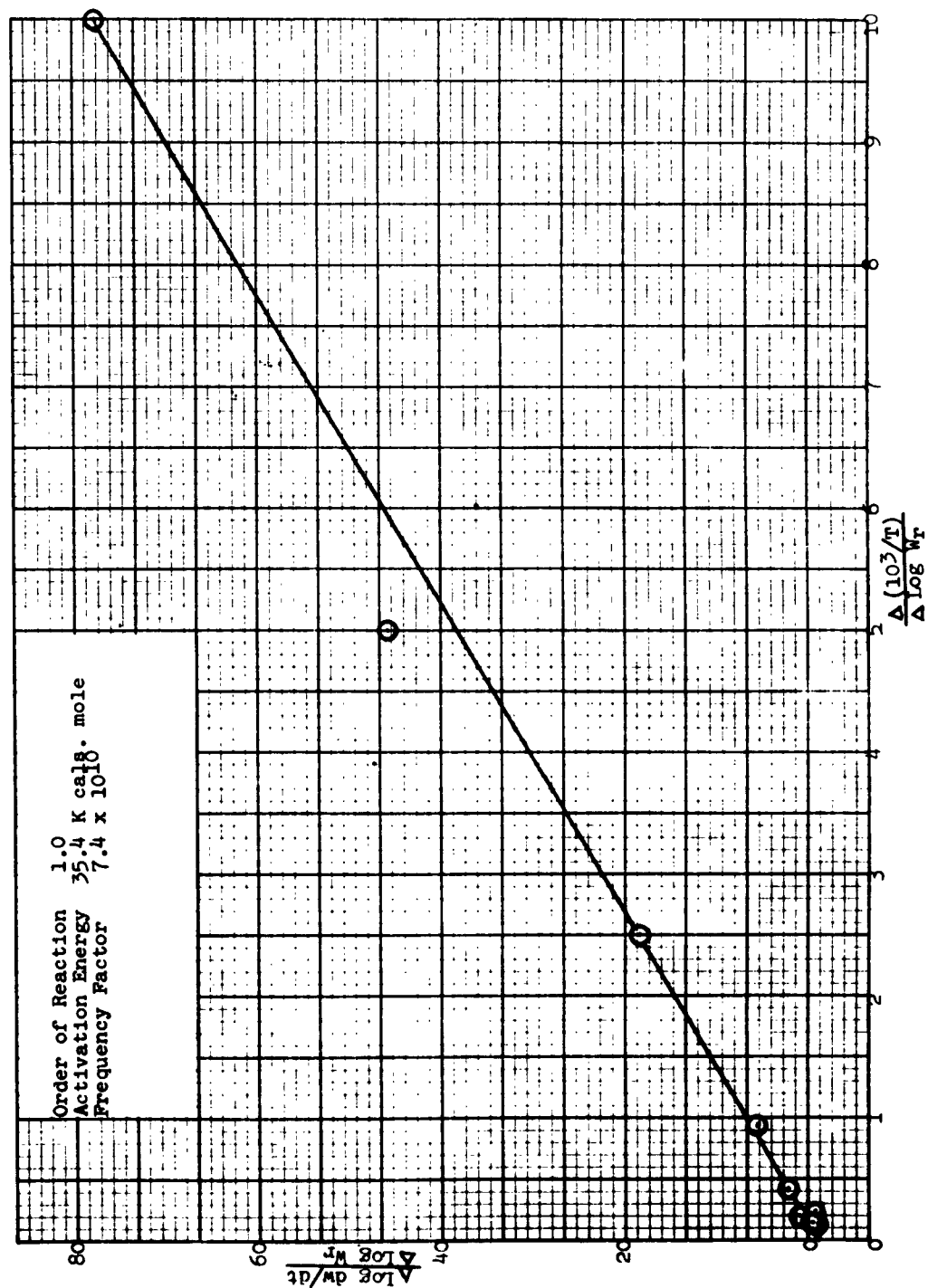


Figure 21. Kinetics of Degradation of Epon 828 Glass Laminate in Vacuum

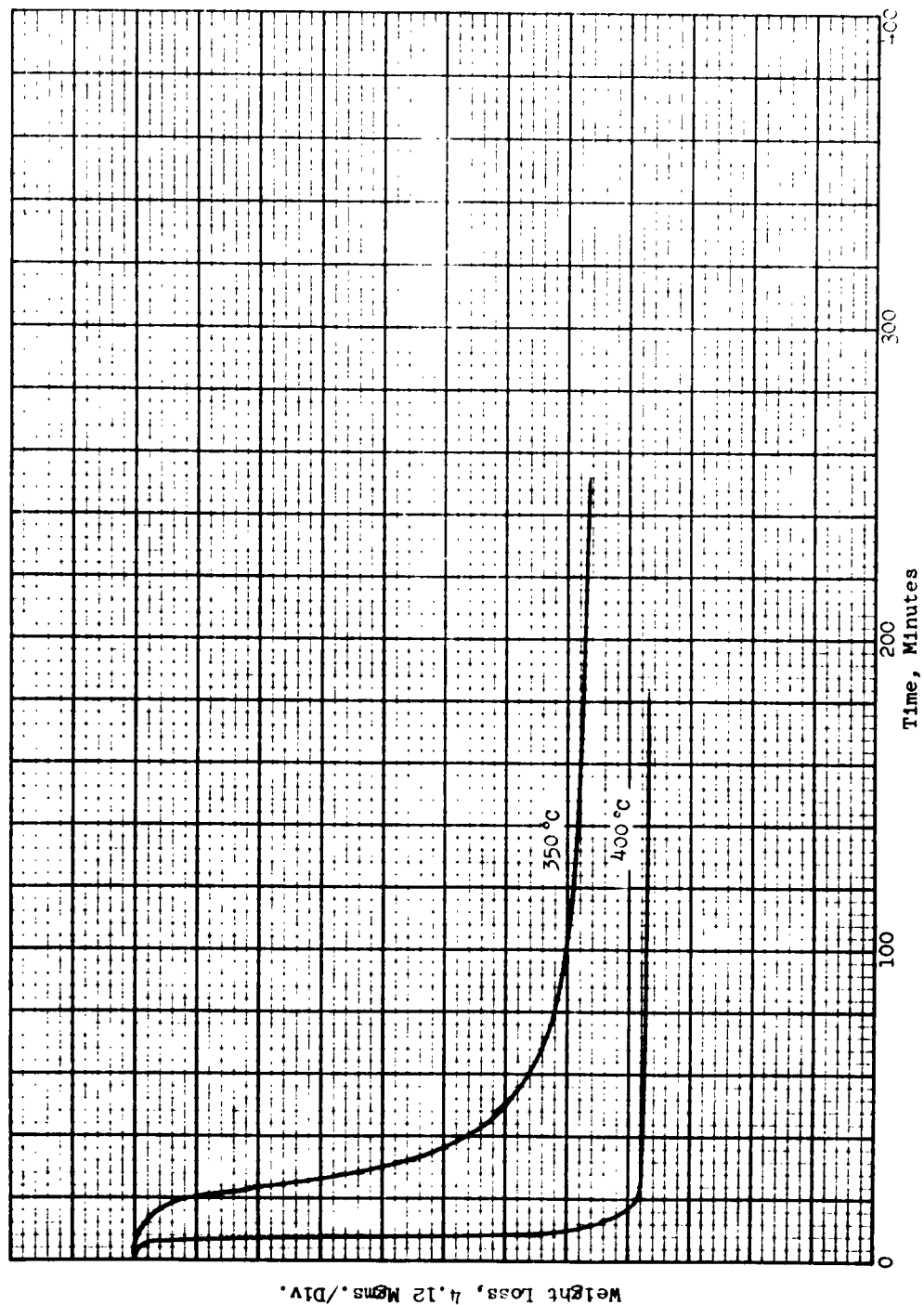


Figure 22. Isothermal Degradation of Epon 828 in Vacuum at Two Temperatures

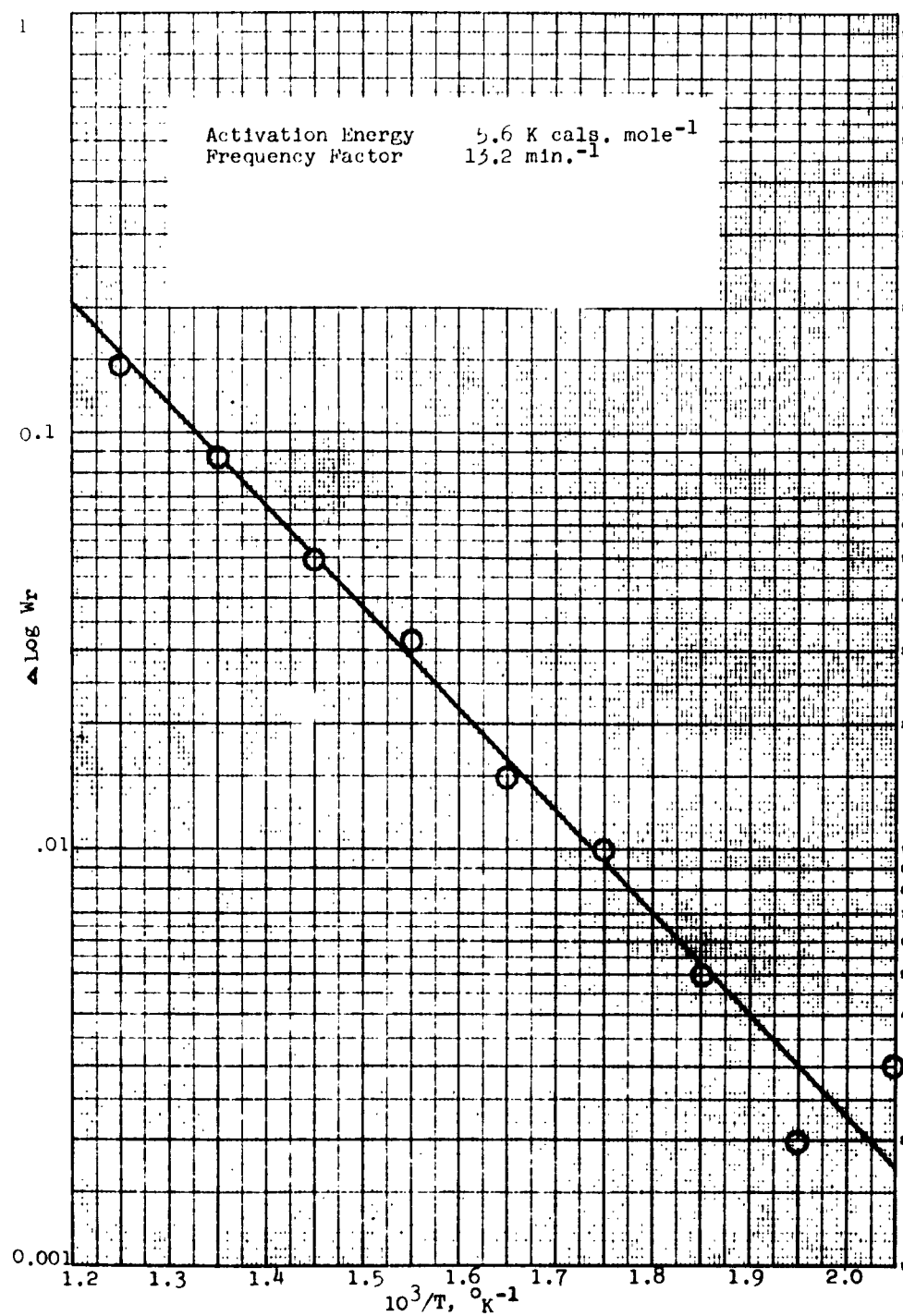


Figure 23. Empirical Kinetic Curve for Resinox Resin

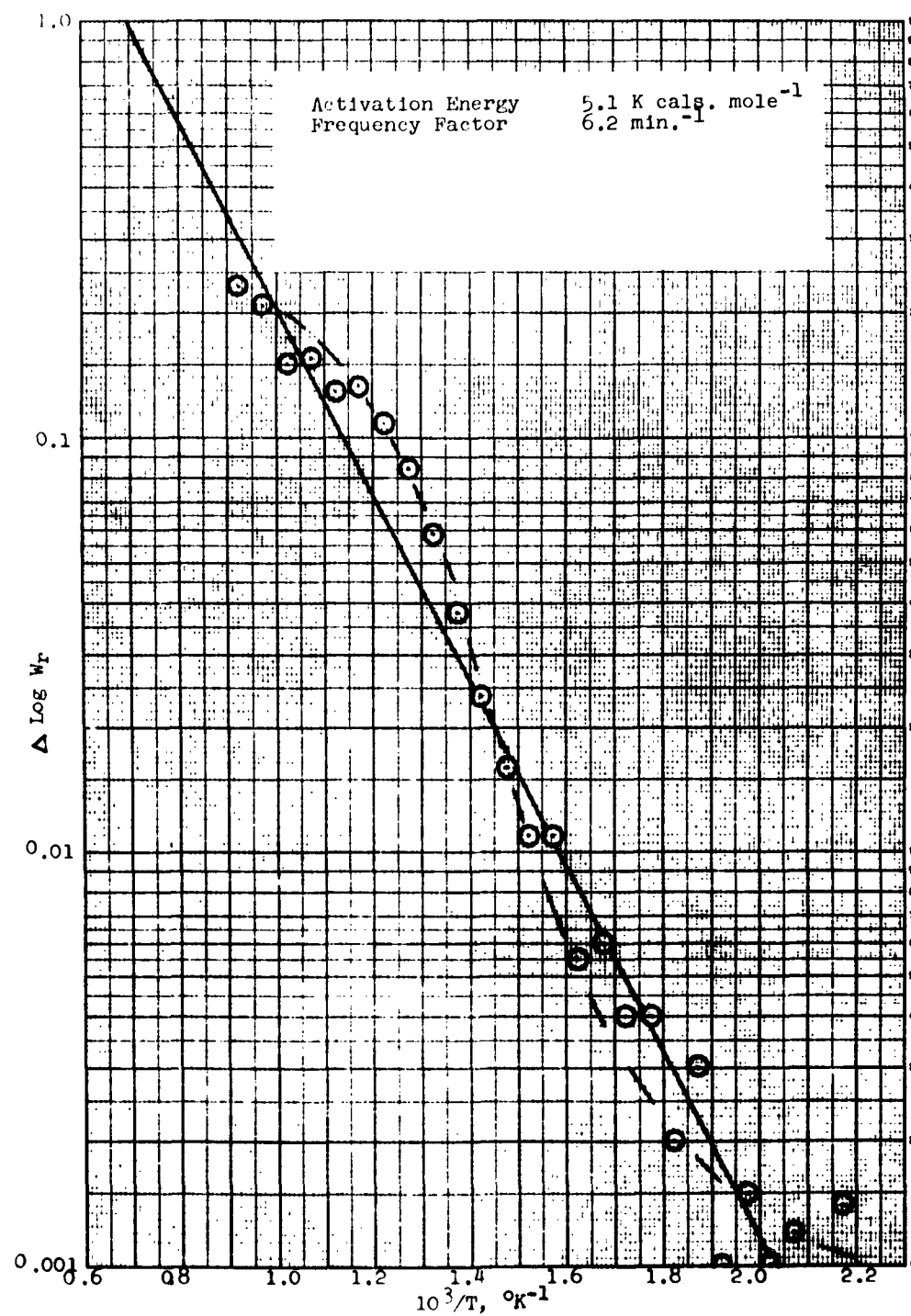


Figure 24. Empirical Kinetic Curve for Resinox Laminate

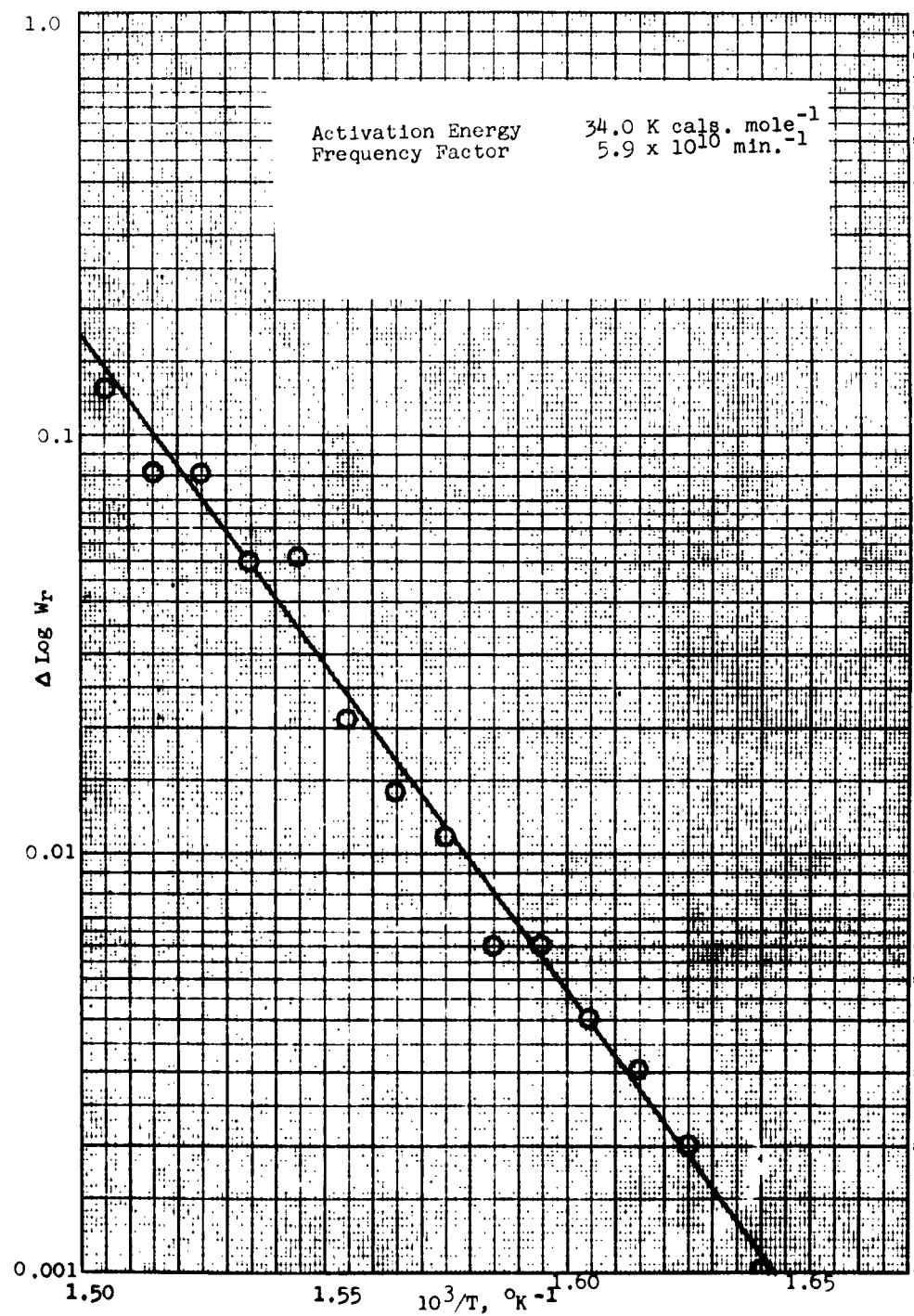


Figure 25. Empirical Kinetic Curve for Epon 828 Resin

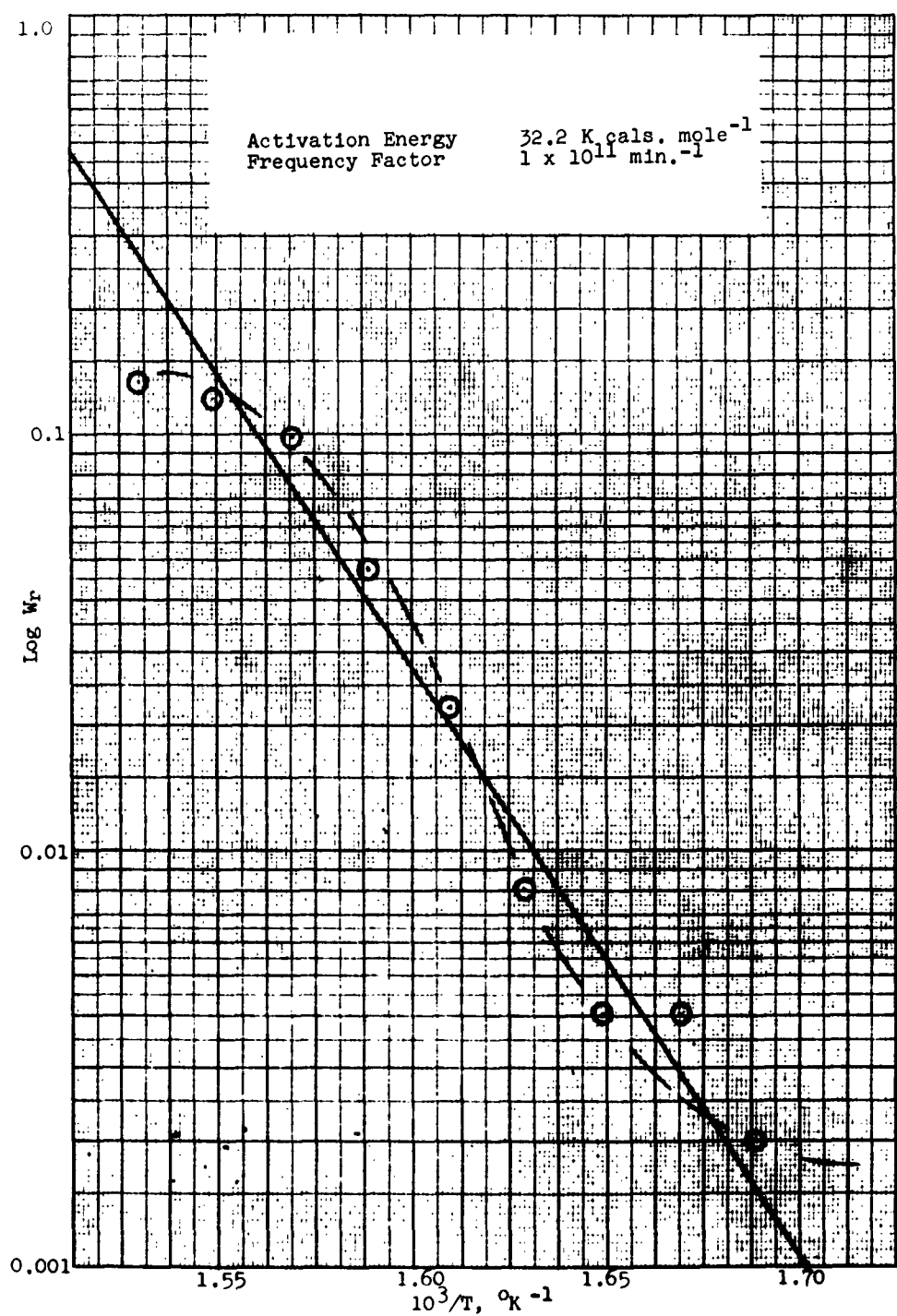


Figure 26. Empirical Kinetic Curve for Epon 828 Laminate

Its disadvantages are that (1) it is as yet partly empirical, derivation from Arrhenius' rate equation not yet being fully accomplished and (2) the curve changes slope, becoming positive near the point of inflection of the TGA curve. The negative linear portion of the curve, used here for kinetic calculations, is believed to have the following equation, perhaps being identical with the secant or tangent of the d (TGA) curve at the point of inflection:

$$(6) \ln (\ln W_2/W_1) = 2 \ln Z^* - \frac{2E^*}{RT} + \ln 2.303$$

$$\text{or} \quad (7) \log (\Delta \log W_r) = 2 \log Z^* - \frac{2E^*}{2.303 RT}$$

The activation energy is then given by:

$$(8) E^* = - \frac{2.303 R (\text{slope})}{2}$$

and the frequency factor by:

$$(9) \log Z^* = \frac{(\text{intercept})}{2}$$

Shown in Table 1 is a comparison of the kinetics constants obtained by the two methods presented here and those found in the literature:

Table 1

Sample	Method of Freeman & Carroll		Wilson E*	Empirical Z*	Literature <sup>(6)</sup>	
	E*	Z*			E*	Z*
Resinox resin	6,530	1.51	5,570	13.2	-	-
Resinox laminate	4,650	0.49	5,120	6.2	-	-
Epon resin	32,600	4.1x10 <sup>10</sup>	34,000	5.9x10 <sup>10</sup>	38,700	8.1x10 <sup>11</sup>
Epon laminate	35,400	7.4x10 <sup>10</sup>	32,200	1.0x10 <sup>11</sup>	-	-

The values of E\* and Z\* shown in Table 1 are average or overall values for the many different reactions which occur during polymer degradations. The significance of kinetic constants obtained from thermogravimetric analysis has also been strongly challenged.<sup>(7)</sup>

3. Thermal Endurance Limit Guare<sup>(8)</sup> suggested a potential method for determining the thermal endurance limit, or temperature below which failure resulting from thermal processes will not occur. This technique will apply whenever exposure of the test material to elevated temperature causes a weight change, and a failure criterion can be correlated with that change in some way.

Suppose, for instance that a plastic structural part thermally degrades when exposed to elevated temperature in such a manner that



a weight loss results. If it is known that the part will fail after a given weight loss, and if the kinetics of the degradation are known, a temperature can be calculated, below which failure will only occur after an unlimited time.

Suppose the rate equation, for example is

$$(10) \quad \frac{dW}{dt} = k W_r$$

where the nomenclature is the same as before.

If a series of test thermal degradations are carried out at different linear rates of temperature increase, such as in the thermogravimetric analyses, a family of degradation curves will be obtained, such that

$$(11) \quad T = h_N t$$

where  $h$  = rate of temperature increase,  $\frac{dT}{dt}$

$N = 1, 2, 3 \dots N$ , the number of the curve

and  $k$  is related to temperature by the Arrhenius equation:

$$(12) \quad k = Z^* e^{-\frac{E^*}{RT}}$$

Integrating equation (10):

$$(13) \quad \ln \frac{W_r}{W_0} = kt$$

and substituting equations (11) and (12) into equation (13),

$$(14) \quad \ln \frac{W_r}{W_0} = \frac{Z^*}{h} T e^{-\frac{E^*}{RT}}$$

or, rearranging

$$(15) \quad T e^{-\frac{E^*}{RT}} = \frac{h}{Z^*} \ln \frac{W_r}{W_0}$$

Now, using the failure criterion that the structure is no longer suitable when  $W_r/W_0$  reaches some arbitrary value, the temperature corresponding to this value on each of the test degradation curves can be easily found. It then becomes possible to plot  $h_N$  vs.  $T e^{-E^*/RT}$  as suggested by (15) and obtain a straight line. The intercept of this curve, corresponding to failure at zero heating rate (i.e., failure after unlimited time) gives the thermal endurance limiting temperature. Below this temperature the failure value should not be reached in a time comparable to the total TGA test time only. This rather restrictive limitation is necessary due to the non-equilibrium conditions occurring in thermogravimetric analysis degradations, which severely limit long-term predictions.

If a failure criterion is given that a specific laminated phenolic structure, such as the Resinox laminate of this investigation, will become unsuitable when a loss of, say,  $1/e = 36.8\%$  of its degradable polymer has occurred, i.e., when  $W_r/W_0 = 0.632$ ; the following results may be obtained. Thermogravimetric degradations in vacuum at two very low heating rates gave the weight loss curves shown in Figure 27. Figure 28 is a plot of  $T_e - E^*/RT$  vs. heating rate,  $h_N$ , showing the temperatures corresponding to failures at the two heating rates taken from Figure 27. Extrapolation in Figure 28 to zero heating rate is seen to specify  $T_0 e^{-E^*/RT_0} = 16.1$ . Solution of this transcendental equation, using kinetic constants obtained by the method of Freeman and Carroll yields  $T_0 = 726^\circ\text{K}$  or  $453^\circ\text{C}$ . Below this temperature, assuming equilibrium conditions and the applicability of the kinetics equations at all temperatures and heating rates, the failure criterion of weight loss  $W_r/e$  should only occur at a time long compared to the total test degradation time.

4. Differential Thermal Analysis Figure 29 shows comparative differential thermal analyses of Epon 828 and Resinox SC-1008 glass laminates in helium. Interpretation of these curves may be facilitated by an expression derived by Murray and White<sup>(9)</sup> relating kinetic constants with peak deflection (maximum degradation rate) temperature,  $T_m$ :

$$(16) \quad Z e^{-E^*/RT_m} = \frac{E^*}{RT_m^2} \frac{dT}{dt}$$

where the symbols have the same significance as before. Using the kinetic constants determined by the method of Freeman and Carroll from Table 1, and the heating rate of  $12^\circ\text{C}/\text{minute}$  utilized to obtain the DTA of Figure 29,  $T_m$  was found to be  $665^\circ\text{K}$  ( $392^\circ\text{C}$ ) for the Epon laminate and  $697^\circ\text{K}$  ( $424^\circ\text{C}$ ) for the Resinox laminate, indicating that degradation peaks should be found near these temperatures, the size, shape and locations of which are subject to instrumental variations as well as degradation rates. Equation (16) may also be expressed in the alternative form:

$$(17) \quad \frac{d(\ln h/T^2)}{d(1/T)} = - \frac{E^*}{R}$$

where  $h = dT/dt = \text{heating rate}$ , as before.

Freeman and Carroll<sup>(10)</sup> have also derived expressions for differential thermal analyses which are linear, with intercepts of  $-n$  and slopes of  $+E/2.303R$  for any unique physical or chemical reaction:

$$(18) \quad \frac{\frac{E^*dT}{RT^2}}{d \ln [K(A-a) - C_p \Delta T]} = -n + \frac{d \ln (C_p \frac{d\Delta T}{dt} + K\Delta T)}{d \ln [K(A-a) - C_p \Delta T]}$$

and

$$(19) \quad \frac{\frac{-E^*}{R} \Delta(1/T)}{\ln [K(A-a) - C_p \Delta T]} = -n + \frac{\Delta \ln (C_p \frac{d\Delta T}{dt} + K\Delta T)}{\Delta \ln [K(A-a) - C_p \Delta T]}$$

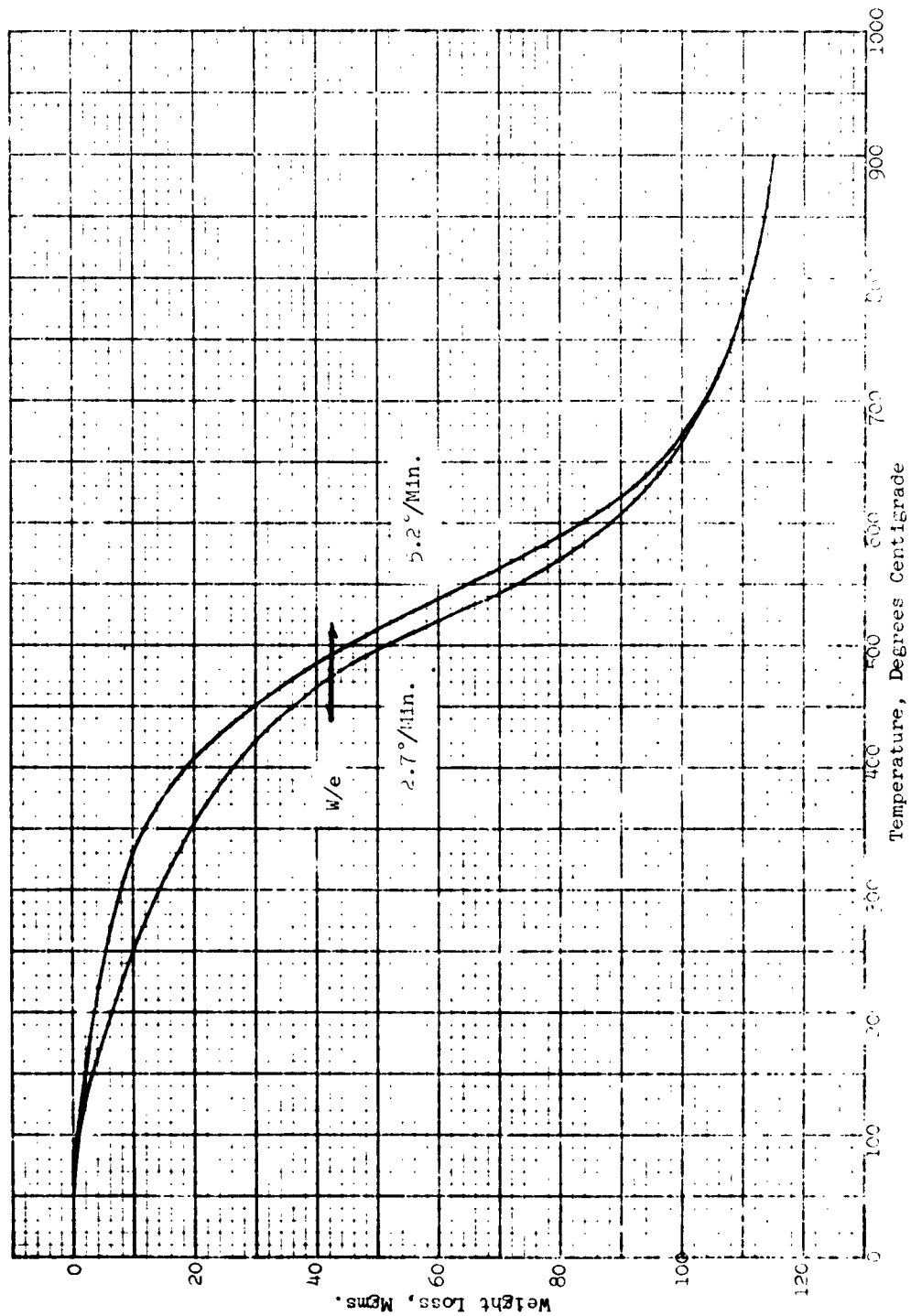
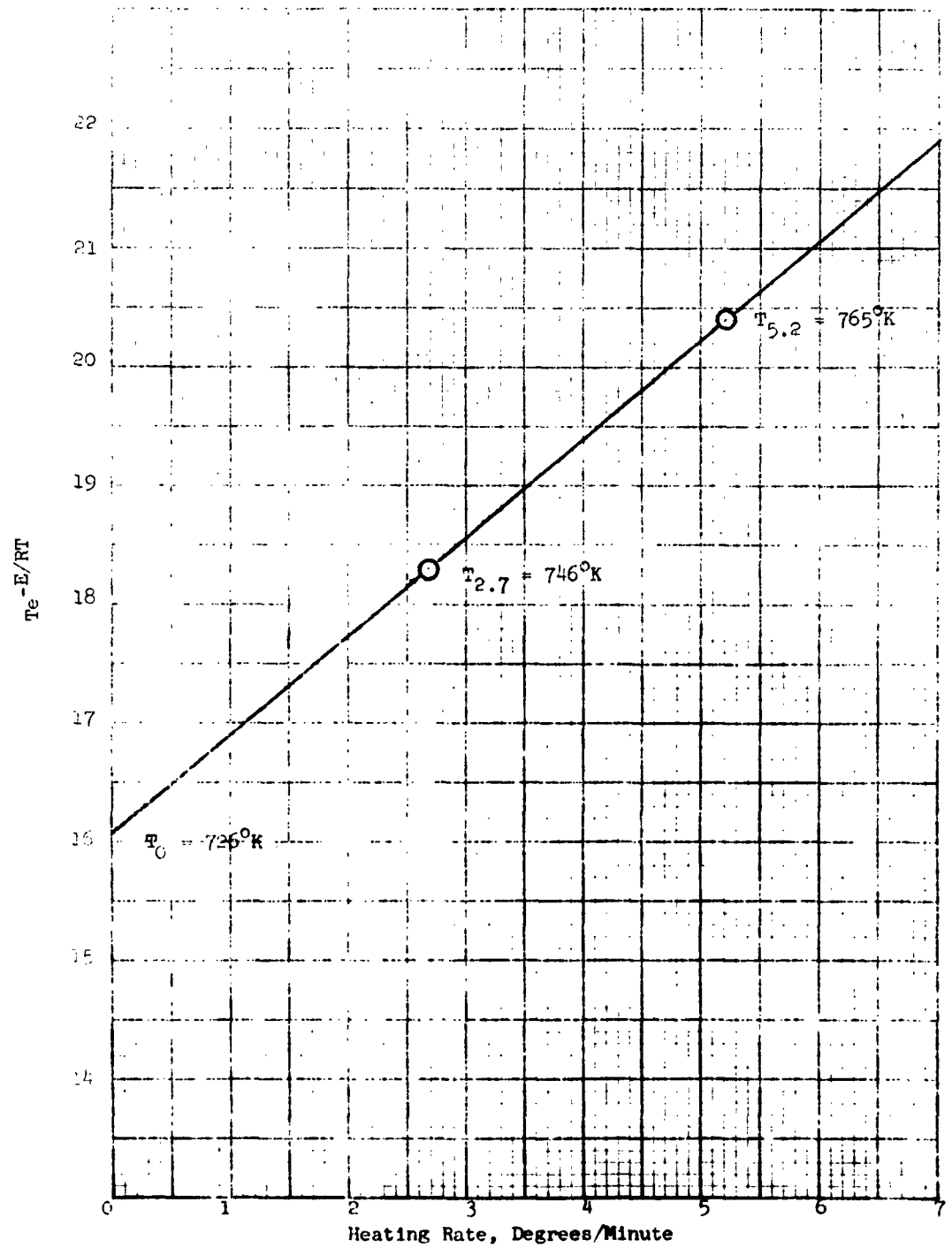


Figure 27. TGA of Resinox Laminate at Two Different Heating Rates



**Figure 28.** Thermal Endurance Limit for Resinox Laminate

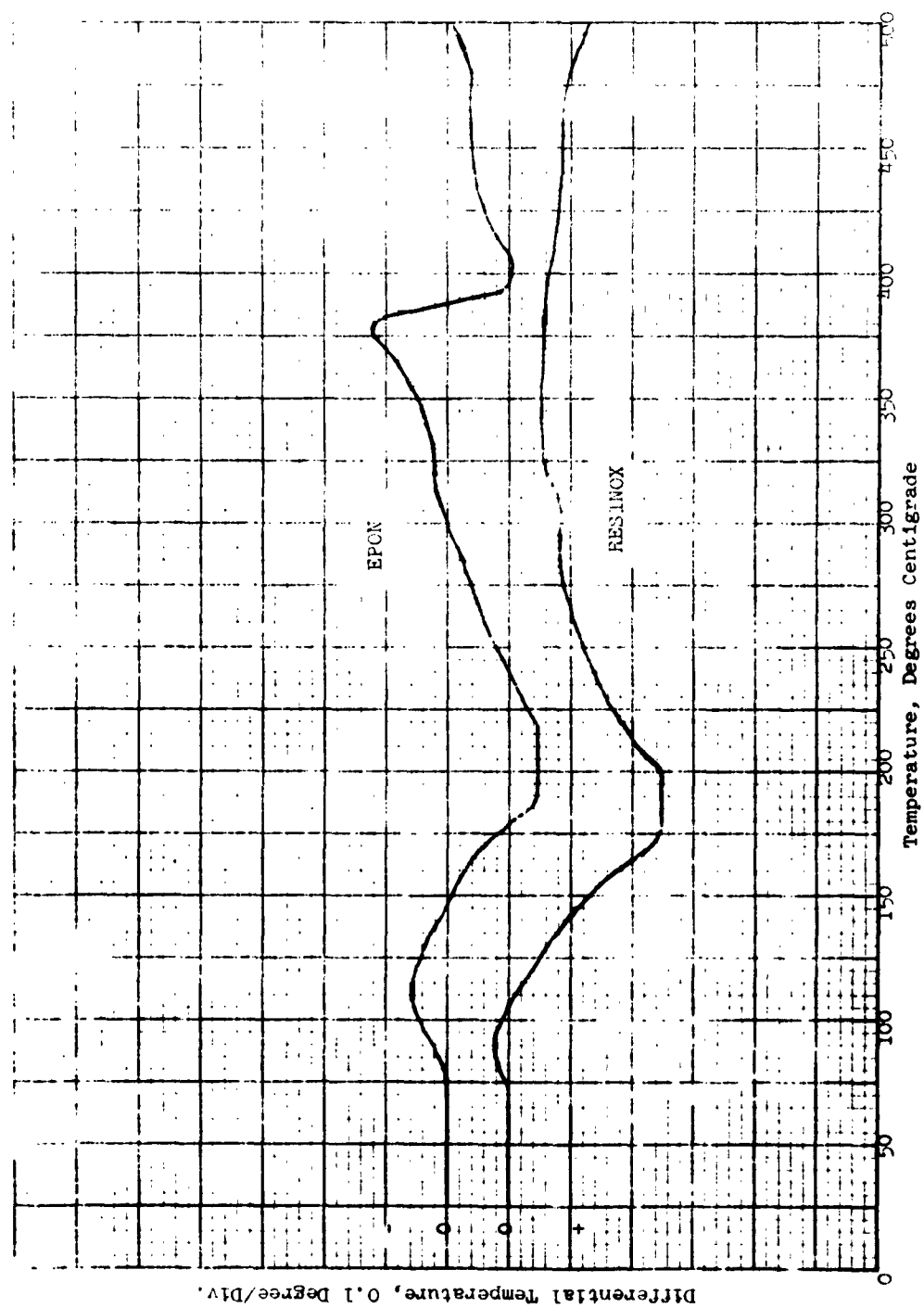


Figure 29. Differential Thermal Analyses of Epon and Resinex Laminates in Helium

where  $K$  = heat transfer coefficient  
 $A$  = area under curve  
 $\Delta T$  = differential temperature at a particular time  
 $d\Delta T/dt$  = rate of change of differential temperature at the point where  $\Delta T$  is measured  
 $C_p$  = total heat capacity of reactant  
 $a$  = area under curve up to time where  $\Delta T$  and  $d\Delta T/dt$  is taken

All the other symbols have the same significance as before.

These latter expressions are valid only where the volume of the reaction mixture does not change appreciably, however, and therefore would not apply to polymers in the range of temperature where degradation to gasses occurs.

### CONCLUSIONS

1. Resinox silicone modified phenolic resin was found to degrade thermally very slowly over the entire temperature range beyond about 250°C, the half-weight loss temperature being about 536°C in a system of linearly increasing temperature of 5°C/minute. Epon 828 epoxy resin degraded similarly up to about 350°C whereupon degradation became very rapid, the half-weight loss temperature being about 388°C.

2. In air, oxidation of the carbonaceous residue is consequent upon thermal degradation, and in the Epon tests may be seen as a distinct second step. Tests in helium and in vacuum were not greatly different. Both Resinox and Epon laminates gave distinctly different TGA curves from those of the pulverized resins, especially in air. This is believed to be due both to variation in sample geometry (diffusion and heat transfer) and to the glass fabric (interfacial areas) and sizing included in the laminates. Very great instrument precision was found to be necessary for reliable TGA runs.

3. The energy barrier to degradation of Resinox resin was found to be kinetically only one fifth as "high" as that for the Epon resin; however, the relative rates of degradation of the two resins must also be described as proportional to the ratio of their frequency factors, i.e., the Resinox resin degrades only a fraction as fast as does the Epon resin.

4. Contrary to reports decrying the accuracy and theoretical significance of thermogravimetric and differential thermal analytical data, it was found that TGA data correlated reasonably well with the literature and was theoretically correlatable with DTA data. An

empirical method for kinetics calculations has also been found which requires only the plotting of log weight change parameters, with no tangent measurements required.

#### RECOMMENDATIONS FOR FUTURE WORK

1. Materials It is recommended that sizings be investigated with respect to their effects on the over-all thermal stability of the laminate in addition to their effects on modulus, etc.

2. Instrumentation It is recommended that further studies be made utilizing simultaneous TGA and DTA instrumentation. Merely the fact of simultaneity is not the important item here, but the added information which may be obtained by ultra-precision and simultaneous records. Such precision might be facilitated by photographic enlargement of the recorder tracings if adequate signal-to-noise ratios are obtained.

3. Theoretical Much of the kinetics data reported in the literature have been largely of academic interest. The reasons for this are that the data are frequently of questionable accuracy or in conflict with other reports, and that the application of kinetic data to many engineering situations has not been widely explored.

It is recommended that studies be made relative to increasing the accuracy and utility of polymer kinetic data, especially that obtained from TGA and DTA. Such data are expected to be of great value in materials selection, structural design, materials and polymer development, stability studies, ablation studies, etc.

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## APPENDIX

### Derivation of an Equation for Direct Calculations of Kinetic Constants from the TGA Inflection Point

Proposed by

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Consultant to MRC

Assume a sample of Weight  $W_0$  at starting time  $t_0$  and initial temperature  $T_0$ , heated at a linear rate,  $h$  degrees/minute, so that

$$T_t = T_0 + ht \quad (1)$$

until the sample disappears or is converted into a char of weight  $W_\infty$

Let  $W$ , defined by

$$W = W_t - W_\infty \quad (2)$$

represent the weight of reactive material present at time  $t$ . Assume that it disappears by a single first order reaction so that

$$\frac{dW}{dt} = -kW = -WZ e^{-\frac{E^*}{RT}} \quad (3)$$

Then

$$\frac{dW}{dT} = \frac{dW}{dt} \frac{dt}{dT} = \frac{1}{h} \frac{dW}{dt} \quad (4)$$

where  $dw/dT$  is the slope on the TGA recording. Taking the second derivative with respect to temperature of equation (4) and equating to zero at the inflection point

$$\begin{aligned} \frac{d^2W}{dT^2} &= \frac{1}{h} \frac{d}{dT} (dW/dt) \\ &= -\frac{Z}{h^2} e^{-E^*/RT} \left( \frac{dW}{dt} + \frac{WE^*}{RT^2} \frac{dT}{dt} \right) = 0 \end{aligned} \quad (5)$$

Whence

$$E^* = \left[ \frac{RT^2}{W} \frac{dW}{dT} \right]_{T=T_{\text{inflex}}} \quad (6)$$

Then

$$Z^* = \left[ \frac{h}{W} \frac{dW}{dT} e^{E^*/RT} \right]_{T=T_{\text{inflex}}} \quad (7)$$

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Unclassified Report

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these materials were investigated. Kinetic constants were calculated for the materials from thermogravimetric analysis results and an empirical method of kinetic calculations is discussed. The thermal endurance limit of Resinox glass laminate was also calculated.

Differential thermal analyses were carried out on Resinox and Epon laminates and theoretical kinetic relationships were used to facilitate their interpretation.

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2. Differential thermal analysis

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